

Medium Range Order (MRO) in Hydrogenated Amorphous Si Detected by a Non-Vanishing Ligand Field Splitting, Δ_{LF} , in Si $L_{2,3}$ Core Level X-ray Spectra

Gerald Lucovsky¹, Gregory N. Parsons¹, Daniel Zeller¹, Rene Lujan², Robert A. Street²

¹North Carolina State University, Department of Physics

2401 Stinson Drive, Raleigh, NC 27695-8202, USA

Phone: +01-919-515-3938 E-mail: lucovsky@ncsu.edu

²Palo Alto Research Center, a Xerox Company, Palo Alto, CA, 94304, USA

1. Introduction and Background

Hydrogenated amorphous silicon alloys, a-Si_{1-x}H_x, with $x \sim 0.08$ to 0.12, display low densities of Si dangling bond defects, and are preferred compositions for applications including absorption regions photovoltaic (PV) devices, and conducting channels in flat panel display thin film transistors (TFTs)[1]. These low defect density a-Si(H) alloys have been deposited by glow discharge (GD) and remote plasma enhanced chemical-vapor-deposition (RPECVD) [2]. There has been much speculation about the near neighbor bonding associated with Si dangling bond densities in the mid-10¹⁵ cm⁻³ regime [3].

Relative concentrations of bonded H have been obtained from IR absorption as a function of substrate temperature, T_s , for (i) monohydride Si-H, and (ii) polyhydride (SiH₂)_n bonding [2], with very different results for GD and RPECVD films. However, when plotted versus the total hydrogen concentration [H], plots are nearly the same [2], suggesting [H], not t_s determines SiH and (SiH₂)_n fractions.

However, deposition and annealing temperatures play a critical role in determining defect densities. Criteria to distinguish between non-equilibrated, and reversible steady state processing have been identified [4], and are significant in explaining relationships between MRO and H-diffusion processes that reduce strain locally [5].

2. Experimental Methods and Results

Amorphous-Si(H) alloys were deposited by (i) GD processes and (ii) RPECVD, onto oxidized crystalline (c-) Si substrates. Two GD films are compared: one deposited at $T_s = 275^\circ\text{C}$ with SiH bonding and a low density of dangling bonds, and a second at 125°C , with (SiH₂)_n bonding and a more than 100 times higher dangling bond density [3].

Figures 1-3 include Si $L_{2,3}$ X-ray absorption spectra a-Si(H) and a-Si films, and for c-Si. Si $L_{2,3}$ spectra represent X-ray transitions from occupied spin-orbit (S-O) split Si 2p core levels at ~ 99 eV to empty Si 4s and 3d states [6]. Si 2p core level holes play a crucial role in these excitations. Transitions are described using charge transfer multiplet (CTM) theory, represented symbolically in as $2p^6 4s^0$ to $2p^5 4s^1$ and $2p^6 3d^0$ to $2p^5 3d^1$ transitions [6].

Spectroscopic detection of multiple $2p^6 3d^0$ to $2p^5 3d^1$ transitions requires MRO order extending to at least third nearest-neighbor correlations associated with specific dihedral angles [7]. These correlations are also evident in valence band spectra as critical point structures associated with symmetry adapted linear combinations (SALC) of atomic states [7]. This scale of MRO is sufficient for a

non-zero ligand field splitting, Δ_{LF} , to be present in Si $L_{2,3}$ spectra. The valence band spectrum of a-Si with only short range order, bond-lengths and bond-angles, has only two $2p^6 4s^0$ to $2p^5 4s^1$ features associated respectively with Si 3s and 3p atomic states. In contrast, the Si $L_{2,3}$ spectrum for a-S(H) with $\sim 10\%$ H, displays multiple $2p^6 3d^0$ to $2p^5 3d^1$ features associated with molecular orbital states, and MRO extending to at least third nearest neighbor atoms.

When core holes and tetrahedral symmetry of Si are taken into account, CTM transitions are from “s-like” ground states with ¹A symmetry to “p-like” final states with ¹T₂ symmetry. Photon absorption requires a non-zero matrix element, $\langle ^1T_{2f} | \mathbf{r} | ^1A_g \rangle \neq 0$; $\mathbf{r}$ is the dipole operator [6].

In the presence of MRO, there is a spectroscopically detectable ligand field splitting, $\Delta_{LF} \sim 1.80 \pm 0.1$ eV, with discrete features in the second derivative Si $L_{2,3}$ spectrum. In the absence of MRO, there are only two 2p to 4s features, each symmetric and separated by the ground state Si $2p_{3/2}$ and $2p_{1/2}$ spin-orbit (S-O) splitting of 0.6 ± 0.1 eV. These two features represent bonding correlations for nearest neighbor bond-lengths and 2nd-neighbor bond-angles. To facilitate comparisons with other experiments [8], x-axis photon energies in Figs. 1 to 3 have been scaled linearly from the soft X-ray regime, ~ 98 eV to ~ 102 eV, to the visible-vacuum ultra-violet (vis-VUV) regime from ~ 2.3 eV to 6.3 eV by calibration with features from c-Si $L_{2,3}$ and epsilon 2 spectra from spectroscopic ellipsometry [9].

Figure 1 compares 2nd derivative Si $L_{2,3}$ X-ray spectra for c-Si and the 250°C GD a-Si(H) film. Qualitative features in these spectra are *equivalent*, but details are different. The c-Si spectrum shows more features in the 2p to 4s regime, whilst the a-Si(H) spectrum shows more strong features in the 2p to 3d regime. Differences within the 2p to 3d regime are explained by noting that the a-Si(H) $L_{2,3}$ spectrum reflects only MRO order, and is not subject to band structure long range periodicity effects as in c-Si. For example, fewer features in the c-Si spectrum are analogous to forbidden reflections in X-diffraction [10].

Figure 2 displays Si $L_{2,3}$ 2nd derivative spectra for (i) the 125°C GD a-Si(H) film, and (ii) an a-Si film prepared by 30°C RPECVD. Each spectral trace displays two symmetric features centered at ~ 2.76 and 3.40 eV with the Si 2p S-O splitting of 0.6 ± 0.1 eV. The two features are *equivalent* to the single feature centered at ~ 3 eV in vis-VUV spectral data [8]. The absence of multiple features between 3.6 eV and 5.6 eV in Fig. 2, and in Fig. 1 of Ref. 11 indicates that $\Delta_{LF} = 0$ for these films. This confirms the

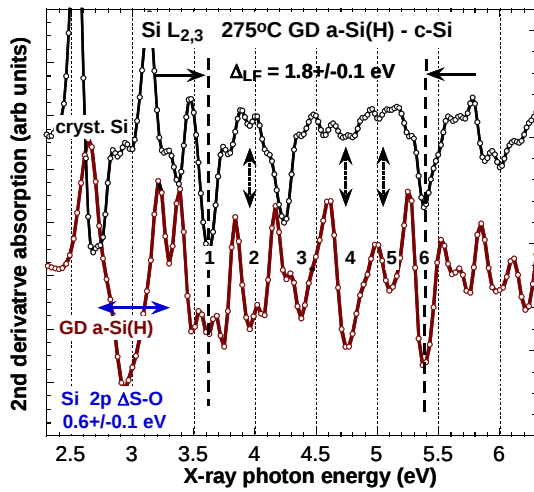


Fig. 1. Comparison between Si 2nd derivative Si L_{2,3} for GD 275°C a-Si(H), and c-Si.

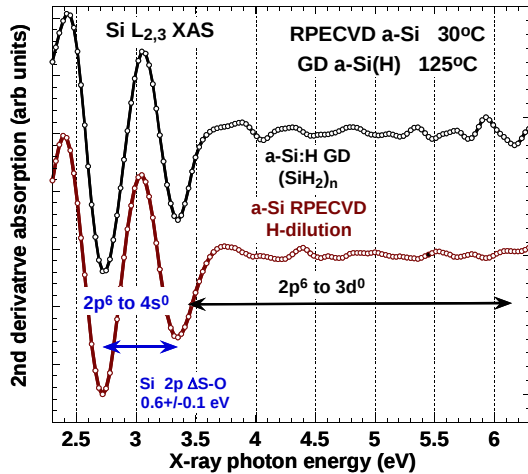


Fig. 2. Comparison between Si 2nd derivative Si L_{2,3} for GD 125°C a-Si(H), and REPCVD a-Si.

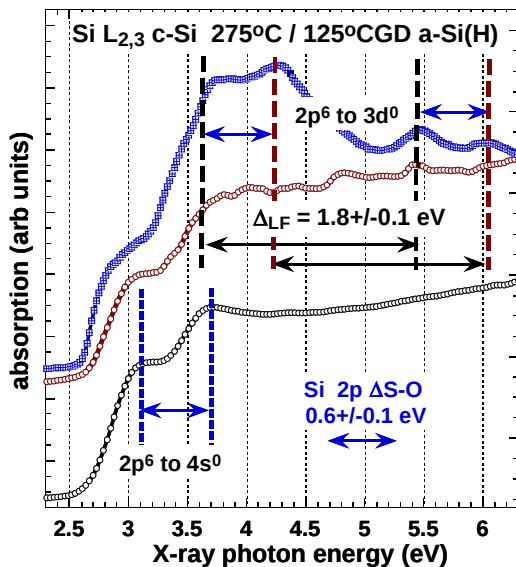


Fig. 3. Si L_{2,3} c-Si, 125°C & 275°C a-Si(H).

absence of MRO order in a-Si films deposited at room temperature. The absence of MRO in the GD 125°C film derives from random dihedral angle correlations in *disordered/curled* dihydride (SiH₂)_n chains.

Figure 3 compares Si L_{2,3} spectra for the a-Si(H) film c-Si and GD films deposited at 125°C and 275°C. Consistent with differences between 2nd derivative spectra compared in Fig. 1, the fewer, but better defined spectral peaks for c-Si give fewer, more distinct features in the Si L_{2,3} spectrum compared with the same spectrum of the 275°C GD a-Si(H) film. Comparing Figs. 1 and 2, there are no significant spectral features in the Si L_{2,3} spectrum of the 125°C GD film in Fig. 3, consistent with absence of MRO.

3. Summary

The most significant aspect of the experimental results is the relationship between MRO in the 275°C GD a-Si(H) films, and low defect densities that are enabling for applications in a-Si:H PV and TFT devices [1,3]. Low defect densities and MRO derive from the ability for H-atoms or protons to diffuse within the a-Si matrix at the higher temperatures, 250 to 300°C, but much more slowly at 125°C. This H-diffusion allows local relaxations in the 275°C film, and these propagate to at least 3rd next-nearest neighbor Si atoms. This atomic *volume amplification factor* means that with ~10 atomic % H, approximately 40 % of the atoms display MRO, exceeding a critical volume percolation threshold of ~16.5%, [11]. A relatively small concentration of Si-H bonds then promotes local strain reduction throughout the film, but not necessarily reduction of macroscopic strain. This combination of macroscopic strain, with localized microscopic strain relief parallels what occurs at Si-SiO₂ interfaces annealed at 900°C [12]. When this analysis is applied to GD films with H-dilution and/or to hot wire deposition, each with 5-6 % monohydride bonding, the percolation threshold for local strain relief is also exceeded, explaining low defect densities [13]. MRO at Si-H sites is likely related to polymorphic precursor effects. H atoms released from Si-H bonds at temperatures ~450 to 700°C, are likely to be nucleation sites for micro/nano-crystallite formation and subsequent growth.

References

1. P.G. LeComber, J. Non-Cryst. Solids 115, 1 (1989).
2. G. Lucovsky, et al., Solar Cells 27, 121 (1989).
3. R.A. Street, et al., Phys. Rev. B 24, 969 (1981).
4. G.N. Parsons, et al., Appl. Phys. Lett. 56, 1985 (1990)
5. D.K. Beigelsen, et al., Phys. Rev. B 20, 4839 (1979).
6. F.M.F. de Groot, et al., Phys. Rev. 41, 928 (1990).
7. F.A. Cotton, Chemical Applications of Group Theory, 2nd Ed. (Wiley Interscience, New York, 1963) Chap. 8.
8. B. Kramer, et al., phys. stat. sol. (b) 49, 525 (1972).
9. T. Yasuda et al., Applied Optics 33, 7435 (1994).
10. C. Kittel, Introduction to Solid State Physics, 8th Ed. (John Wiley, New York, 2005), Chap. 2.
11. H. Scher, et al., J. Chem. Phys. 53, 3759 (1970).
12. J.T. Fitch, et al., J. Vac. Sci. Technol. B 7, 775 (1989).
13. S. Guha, et al., Appl. Phys. Lett. 74, 1860 (1999).