#### Spectroscopic detection of medium range order in device-grade a-Si:H:

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## 1. Introduction

Hydrogenated amorphous silicon, a-Sil-xHx, x~0.1±0.02, is used in photovoltaics (PV) and thin film transistors (TFTs). This alloy has been deposited by the glow discharge method. remote plasma-enhanced chemical vapor deposition, and reactive magnetron sputtering [1]. Two conditions are necessary for low Si dangling bond densities: (i) a bonded mono-hydride, Si-H, concentration of 8 to 12%, and (ii) deposition, and/or a post-deposition anneal at ~250-300°C [2]. Second derivative Si L2,3 X-ray absorption spectroscopy is used to confirm medium range order (MRO) beyond the short range order of continuous random networks by observation of ligand field split Si 3d-state features. MRO was not found in a-Si, and in GD films deposited at 125° with high defect densities. Annealing during, or after deposition redistributes H ions/protons to reduce strain locally resulting in markedly low defect densities.

# 2. Medium Range Order

Low defect density alloys have been deposited by the glow discharge method, remote plasma-enhanced chemical vapor deposition, and reactive magnetron sputtering. There has been speculation about the near-neighbor bonding that promote a low-density of Si dangling bonds. This defect density extends to the mid- $10^{15}$  cm<sup>-3</sup>. The role of bonded-H in mono-hydride Si-H arrangement in the x ~0.08 to 0.12 composition window is addressed. X-ray absorption spectroscopy at the Stanford Synchrotron Research Lightsource, combined with diffusion studies explains the low defect density. a-Si:H alloys were prepared by glow discharge deposition on crystalline Si substrates with 10 nm

SiO2 interfacial layers to prevent crystalline formation. Spectra are obtained for one film deposited at 275°C with a low density of Si-atom dangling bonds, and a second at 125°C, with Si poly-hydride (SiH2)n bonding and higher defect density.

In the presence of MRO, there is a spectroscopically detectable ligand field splitting,  $\Delta$ LF, with six transitions [3]. In the absence of MRO, there are only two 2p to 4s transitions, each symmetric and separated by the ground state Si 2p3/2 - Si 2p1/2 spin-orbit splitting of 0.6±0.1 eV. The x-axis photon energies in Figs. 1 and 2 have been scaled linearly from the X-ray regime, ~98 eV to ~102 eV, to the visible-vacuum ultra-violet regime to 2.3 eV to 6.3 eV to provide comparisons with other experiments; reflectivity and ellipsometry.

Figure 1 compares Si L2,3 spectra and 2nd derivative L2,3 for the a-Si(H), ~10% H, deposited at 275°C. Qualitative features in the two spectra are similar: the edge at ~2.6 eV, and a weaker feature at ~3.7 eV marks the onset of 2p to 3d transitions. Two pairs of features, split by the Si 2p spin-orbit splitting of  $0.6\pm0.1$  eV, identify the ligand field spitting of  $1.7\pm0.1$  eV for GD 275 °C a-Si(H).

Figure 1 also displays Si L<sub>2,3</sub> and 2ndderivative spectra for (i) the 125 °C GD a-Si(H) film. The 2nd derivative spectrum displays two symmetric features centered, respectively, at ~2.76 and 3.40 eV with a Si 2p spin-orbit splitting of  $0.6\pm0.1$  eV.13) These are from the spin-orbit split components of the Si 2p core level. The absence of features between 3.6 eV and 5.6 eV, indicates that there is



Fig. 1. Si L2,3 and 2nd derivation L2,3 for GD a-Si(H) deposited at 275 and 125°C

### 3. Discussion

The most significant aspect of the experimental results is a 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. Low defect densities and MRO arise from the ability for H-ions/protons to diffuse within the a-Si matrix at higher temperatures, ~250°C, but more slowly at 125°C.5) Hydrogen diffusion allows local relaxations in the 275°C film, and these extend to at least 3rd next-nearest neighbor Si atoms. The relatively small concentration of Si-H bonds promotes local strain reduction throughout the entire film, but not necessarily a reduction of macroscopic strain. This combination of macroscopic strain, with local microscopic strain relief. Figure 2 contains a schematic representation of the molecular cluster in a-Si(H) that means it is not a covalent random network, CRN, material.

The distribution of H atoms around dangling bonds in lightsoaked a-Si:H, i.e., the Staebler-Wronski effect SWE, was addressed by electron-nuclear double resonance (ENDOR) [4]. In contrast to previous electron spin echo envelope modulation (ESEEM) studies it was demonstrated that the distance between bonded H atoms and Si dangling-bond defects was ~0.3 nm [5]. In a 1998 paper [6], a mechanism for charged defect formation at hydrogenated Si-SiO<sub>2</sub> interfaces, and in thin film a-Si:H that occurred for ~0.4 nm distances between Si-dangling bonds and H-atoms trapped in weak Si-Si bonds.[6] Generation of metastable neutral and charged defects in a-Si:H by reactions involving changes in H-atom bonding arrangements has been studied by ab initio calculations applied to small molecular clusters. A unified defect generation model was proposed in which reactions pathways for photo-induced defect generation in PV devices are initiated by hole-electron pair recombination and/or deep trapping. Reactions or pathways were proposed for intrinsic processes in a-Si(H) involving only Si and Hatoms; these are presented in Fig. 2 [6] In the PV devices, defect generation includes the creation of neutral and charged defects, and involves displacive motion, rather than diffusive hydrogen motion, ensuring defect metastability. Specifically, Fig. 2 includes the cluster associated with

MRO and the 2nd and 3rd nearest neighbors of the H-atom of the Si-H bond. The symmetry of nearest neighbor Si atoms back-bonded the Si-H bond, establishes the ordering and magnitude of the dihedral angles defining MRO. The figure also includes the reactions equations for defect generation by hole trapping, and defect neutralization by electron capture. The low density of dangling bonds in asdeposited pristine a-Si(H) with 5-10% H is determined by the growth process and annealing and kinetics of defect formation. Paradoxically, this same center is the source of the kinetic effects that promote dangling bond formation under intense white light illumination, i.e., the SWE.Finally, the insights in this paper with regard to local molecular clusters, and the mechanism for the SWE suggest ways to possibly ways that magnitude of the density of defects generated by light-soaking is enhanced by O- and N-atom impurities. Each of these more strongly electronegative elements can replace Si-H bonds with either Si-OH or SiNH bonds that are stronger than the Si-H bond. If the O- and N-atoms were in the matrix, and the Si-H is the apex of the cluster, this would why O- and N- impurities increase the SWE [7]. The microscopic aspect that is important is the Hbonding between the H and either the O- or N-atom. References

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Fig. 2. Molecular structure reactions for SWE in a-Si(H) with low O- and N- impurities,



Fig. 2. Local molecular reactions for SWE in a-Si(H) with high concentrations ( $\sim 10^{-19}$  cm-3) of O- and N- impurities,