Studies of the Structure of Amorphous Silicon Solar Cell Materials and Devices Using Surface Analysis Techniques

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Abstract

Thin film hydrogenated amorphous silicon solar cells have been improved significantly through research, development and manufacturing since their discovery twenty years ago, but there are still a number of fundamental problems and issues that must be resolved before they can reach their full potential. There is still a significant lack of knowledge about the structure and bonding of hydrogenated amorphous silicon and the role these factors play in determining both its performance and stability in devices. This paper will show how ultra high vacuum surface analysis techniques can be used to study the structure and bonding of hydrogenated amorphous silicon solar cell materials and devices and how they can be applied to studies of such practical problems as the Staebler-Wronski effect.

1 INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) is a relatively new material which, since its discovery just on twenty years ago, has been the subject of intensive research with efforts focusing on producing materials for solar cells and electronic devices. Although some success has been achieved in these areas, amorphous silicon has so far failed to achieve the high expectations which were held for it two decades ago. This material still offers the prospect of good efficiency and low cost solar cells, however its application is impeded by a number of problems, including photodegradation or the Staebler-Wronski effect [Kazmerski, 1989; Luft et al., 1991]

One approach to overcoming these problems is to obtain a better understanding of the relationship between the structure and the properties of a-Si:H and the role these factors play in determining its performance and stability in devices. Ongoing advances in computer software, materials preparation and ultra-high vacuum characterisation techniques have allowed remarkable progress to be made in the study of disordered materials, both theoretically and experimentally. Two particularly useful characterisation techniques for studying such materials are Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). They not only give information on the elemental composition and chemical environment of the surface of the material but also the electronic structure of the surface region, including the valence band structure. As the valence band electrons are most affected by any change in the structure or bonding of a material, it is the photoelectron or Auger spectra that involve valence electrons which can be expected to provide the most information about such changes. This paper will show how ultra high vacuum surface analysis techniques can be used to gain a wide variety of information about device quality a-Si:H solar cell material including chemical information, the nature of the structure and bonding and the role these factors play in determining device performance and stability. It will also show how these techniques can be applied to such practical problems as the Staebler-Wronski effect (SWE).
1.1 The use of UHV Characterisation Techniques to Study the Chemical Composition of a-Si:H Solar Cell Materials and Device Structures

Auger electron spectroscopy and x-ray photoelectron spectroscopy have long been used for the chemical fingerprinting of the surface of materials [Carlson, 1976; Seigbahn, 1973]. There are four “chemical” questions that may be answered from the analysis of a material using AES or XPS. What elements are present? How much of each element is present? To what other atoms is an atom of a given element bonded? How is each given element bonded to other elements? It is because of the wealth of chemical information about the surface of a material that is available from these techniques that they are widely used in the semiconductor industry for material characterisation and troubleshooting problems in devices. There are very few other techniques which can easily give such reliable information about the chemical composition of materials and they are therefore invaluable tools for the chemical characterisation of different a-Si:H solar cell materials. As well as the chemical characterisation of different types of a-Si:H material, XPS and AES, in conjunction with noble ion sputter depth profiling, can be used to gain a great deal of useful information about the structure of complete a-Si:H solar cell devices.

An example of the usefulness of these techniques can be seen from our previously reported work [Jennings et al., 1988] using XPS depth profiling to study a-Si:H solar cell devices deposited on stainless steel substrates. During the late 1980’s stainless steel was a popular substrate for a-Si:H solar cells. At that time there was considerable discussion in the literature about the best method of preparing stainless steel for use in a-Si:H solar cells. In order to determine the best type of stainless steel for use in a-Si:H solar cell devices and the best method of preparing it we studied three common types of stainless steel, 304, 316 and 321, and different ways of preparing the substrate. A-Si:H films were deposited onto the different types of stainless steel and the performance of the subsequently fabricated devices were compared for the different substrates and preparation techniques. Considerable differences were found between the performance of the a-Si:H devices prepared on different stainless steel surfaces which had been prepared in different ways.

XPS depth profiling of the a-Si:H/substrate interface was able to clarify the differences in performance observed. Figure 1 shows a typical XPS depth profile of an a-Si:H films deposited on a 321 stainless steel substrate prepared using what was found to be the optimal preparation technique. From Figure 1 it clear that devices made in this way have a predominantly Cr oxide interface between the a-Si:H and the stainless steel substrate. The main difference between the films prepared on the different stainless steel substrates in the study was the thickness of this oxide interface. A direct correlation was found between the stainless steel grades with the thinnest oxide layer at the interface and those devices that had the best performance. Therefore using XPS depth profiling it was possible to provide a reason for the differences in performance of a-Si:H devices prepared on different types of substrates and to use this understanding to optimise the substrate preparation technique.

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**Figure 1:** XPS depth profile for a-Si:H on 321 stainless steel.
1.2 The use of UHV Characterisation Techniques to Study The Structure and Bonding of a-Si:H Solar Cell Materials

Auger electron spectroscopy and x-ray photoelectron spectroscopy not only give information on the elemental composition and chemical environment of the surface but also the electronic structure of the surface region, including the valence band structure. They can provide direct information about the energy distribution of the occupied states in the solid. Electron energy distribution curves of the valence electrons are replicas of the occupied valence band density of states (VBDOS) and thus reflect changes in the electronic structure of a-Si:H due to changes in the structure and bonding of the material. These changes are often not easily seen or measured using core level XPS or AES or even any other technique. AES and XPS are therefore useful techniques for studying a number of the properties and problems associated with a-Si:H solar cell materials.

A typical survey (0 to 1253 eV) x-ray photoelectron spectrum from an a-Si:H sample contains a number of discrete peaks in the energy distribution. These include core level photoelectron and Auger lines, valence band Auger lines and the XPS valence band (XPS VB). It is the energy position and area under the core level XPS lines that are used to gain the chemical information such as that used in the studies described in section 1.1. On the other hand, for the XPS and AES valence band lines, it is the shape of the lines themselves that contain the information about the valence band densities of states. The full x-ray photoelectron spectrum from an a-Si:H sample shows three main features that can be used to determine the VBDOS, the \( \text{L}_{2,3}\text{V} \) Auger line at approximately 45eV, the \( \text{L}_{2,3}\text{VV} \) Auger line at approximately 90 eV and the XPS VB in the region from approximately 1240 to 1253eV. It is these three structures that will be the focus of this work.

Brockman and Russell [1980] have shown that experimental \( \text{L}_{2,3}\text{VV} \) and \( \text{L}_{1}\text{L}_{2,3}\text{V} \) Auger spectra can be treated numerically to obtain an indication of the surface VBDOS. They have shown that the shape of the \( \text{L}_{1}\text{L}_{2,3}\text{V} \) lineshape reproduces the DOS reasonably well, while suppression of the \( s^p \) and \( s^8s \) states in the \( \text{L}_{2,3}\text{VV} \) line distorts that lineshape considerably and it only appears to reflect a partial density of states. Srinivasan [1990] has shown that the XPS VB line directly reflects the partial DOS of silicon sites. This assertion is based on the argument of Reichardt et al., [1983] that the partial hydrogen 1s cross-section is negligibly small at energies beyond 120eV. Various workers [Madden, 1981; Madden and colleagues, 1982; Laznica, 1979; Zajac and Bader 1982; Lund et al., 1994, 1997] have previously demonstrated that AES can be used to indirectly assess the affect of disorder and hydrogen in a-Si:H and to investigate the local VBDOS in a-Si:H. Ching and colleagues [1979] have shown using continuous-random-tetrahedral-network structural models of a-Si that the local electronic DOS for a-Si:H depends on the hydrogen content and hydrogen bonding configuration. They also suggest that as a-Si is hydrogenated the Si 3s-electrons localise more than the 3p-electrons. We have previously reported methods which enable x-ray excited Si \( \text{L}_{2,3}\text{VV} \) and Si \( \text{L}_{1}\text{L}_{2,3}\text{V} \) Auger spectra to be numerically treated routinely to obtain a good indication of the Si VBDOS for a-Si:H [Lund et al., 1994, 1997]. We have also recently been able to develop similar techniques for the XPS VB line.

Previous experimental studies, such as those above, suggest that whilst hydrogen content and disorder cannot be directly identified by core level XPS or AES, in the case of a-Si:H they can be identified through their influence on the VBDOS as reflected in the shape of the Auger and photoelectron valence band spectra. This is achieved by comparing calculated theoretical VBDOS for various models of a-Si:H structures with experimental Auger and XPS VB spectra. We have previously shown [Lund et al., 1994, 1997, Clare et al., 1996a] how we can successfully calculate the valence band densities of states for a set of simple models of a-Si:H using the molecular orbital software package MOPAC [Stewart, 1990]. The results compare well with the experimental Auger and XPS VB spectra. By using models of a-Si:H with and without a number of hydrogen atoms removed, or with Si bonds capped to represent crystalline silicon, we were able to show how the calculated VBDOS could contribute significantly to a qualitative understanding of the effects of both disorder and hydrogenation on various crystalline and amorphous silicon surfaces using Auger and XPS valence band lines. This can then give a great deal of information about device quality amorphous silicon solar cell materials which is not available from core level Auger and XPS lines including information on the effects of disorder and hydrogenation on.
Figure 2 shows the numerically treated experimental L_{2,3}VV, L_{1}L_{2,3}V and XPS VB lines for c-Si, a-Si and a-Si:H surfaces as well as the theoretically calculated VB DOS for models of c-Si and a-Si:H surfaces. Each part of the figure has all the surfaces plotted on the same axis for comparison. Figure 3 shows the same Si L_{1}L_{2,3}V Auger spectra as in part c of Figure 2 by itself in order to enable the differences in the three types of material to be seen more clearly. The differences between the materials in Figure 3 are reflected in the spectra in the other three parts of Figure 2. Disordering the surface of c-Si results in a number of changes to the VB DOS which are reflected directly in the L_{1}L_{2,3}V Auger spectra of Figure 3 (and the other spectra of Figure 2). These changes have been discussed in more detail in our previous publications [Lund et al., 1994, 1997] and will be reviewed here to demonstrate the type of information available from such studies.

![Figure 2](image)

**Figure 2:** (a) The theoretically calculated VB DOS for models of c-Si and a-Si:H surfaces; (b) numerically treated experimental L_{2,3}VV, (c) L_{1}L_{2,3}V and (d) XPS VB lines for c-Si, a-Si and a-Si:H surfaces. Each part of the figure has all the materials plotted on the same axis for comparison. The solid line is c-Si, the long dash is a-Si and the short dash is an a-Si:H sample.

![Figure 3](image)

**Figure 3:** Figure 3 shows the same Si L_{1}L_{2,3}V Auger spectra as in Figure 2 part c by itself in order to enable the differences in the three types of surface to be seen more clearly. The solid line is c-Si, the long dash is a-Si and the short dash is an a-Si:H sample.

From figure 3 it can be seen that ion bombardment of c-Si, to produce disordering (or amorphousness) in the surface, results in an enhancement in the high energy portion of the spectrum near features I and II and there is a noticeable change in the height of the shoulder at III. Also the broad rounded feature at V and VI in the ordered spectrum becomes sharper after disordering, with feature VI appearing as a shoulder. The spectrum changes further after hydrogenation of the surface by hydrogen ion bombardment with a significant reduction in the high energy region (features I and II), with all the other regions showing a marked increase, especially features IV and VI. These changes can be interpreted in the light of the theoretical modeling and the work of others [Madden et al., 1983; Nelson et al., 1986; Ching et al., 1979]. The changes observed on disordering reflect an increase in the number of p-like states in the top of the valence band (peaks I and II), and a decrease in order states deeper in the band (peak III), due to an increase in dangling bonds in the surface. The changes observed after hydrogenation show a reduction in the states at the top of the band (I and II) due to tying off of the dangling bonds and the introduction of new states (III - VI) deeper in the band due to the formation of Si-H bonds. These changes are reflected in each of the three experimental valence band spectra of Figure 2 and clearly give a good method of monitoring changes in disorder or hydrogenation in a-Si:H solar cell materials.

Nelson and co-workers [1986] have used the L_{2,3}VV Auger line to analyse a-Si:H produced by hydrogen ion implantation in silicon single crystals (for analytical standards), and glow discharge (GD) produced a-Si:H thin films (fabricated for solar cell applications) in order to obtain a semi-quantitative measure of the hydrogen concentration in a-Si:H samples. Hydrogen concentrations were confirmed by infra-red spectroscopy and secondary ion mass spectrometry (SIMS) with samples having hydrogen contents in the range of 10^{16}-10^{18} atoms cm^{-3}. The Si L_{2,3}VV Auger line was separated (decoupled) into its underlying component peaks following the model of Jennison [25]. Correlations between the areas of the component peaks and the known hydrogen content resulted in a semi-
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quantitative method of determining the hydrogen concentration. They were able to show that Auger lineshape analysis using the decoupled components of the Si L$_{2,3}$VV spectrum may be used both as a qualitative probe of changes to the VBDOS as well as a semi-quantitative monitor of the amount of hydrogen in a-Si:H samples.

We have been able to extend the method of decoupling to the L$_{2,3}$VV, L$_{1,2}$V Auger and XPS VB lines in a manner similar to that used by Nelson and colleagues [1986] for the L$_{2,3}$VV line [Lund et al., 1997]. Typical decouplings of the L$_{2,3}$VV, L$_{1,2}$V Auger line and XPS VB lines are shown in Figure 4. By a similar application to disordered and hydrogen bombarded c-Si (111) samples and thin films produced by glow discharge for solar cell applications we have shown the decoupled components of the Si L$_{1,2}$V line to be very sensitive to changes in the DOS arising from disorder and hydrogen incorporation. Figure 5 shows the comparison of the decoupled components of the L$_{1,2}$V Auger line for c-Si, a-Si (disordered c-Si) and a-Si:H (disordered and hydrogen ion bombarded c-Si) samples. The areas of these components under the Si L$_{1,2}$V Auger line are shown in Table 1. By using the ratio of the areas of the component peaks (IV+V+VI) to those of the peaks (I+II) it can be seen (Table 1) how a semi-quantitative measure of hydrogenation and disorder is possible. In this way we have shown [Lund et al., 1997, Walker et al., in press] that the L$_{1,2}$V line is able to be used to effectively semi-quantitatively monitor changes in a-Si:H due to both disorder and hydrogenation. Work we have recently completed shows this to also be true of the XPS VB lines.

![Figure 4: Typical decouplings of the a) L$_{2,3}$VV, b) L$_{1,2}$V Auger line and c) XPS VB lines of a-Si:H samples. The measured spectrum is shown as a solid line while the decoupled component curves are shown as dashed lines.](image)

**Table 1:** Areas of the decoupled components under the Si L$_{1,2}$V Auger lines of Figure 5 for an ordered c-Si (111) sample then the same sample after disordering and hydrogen ion bombardment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(I+II)</th>
<th>III</th>
<th>IV</th>
<th>(IV+V+VI)</th>
<th>(I+II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ordered c-Si(111) (Rearnealed)</td>
<td>0.34</td>
<td>0.41</td>
<td>0.00</td>
<td>0.25</td>
<td>0.75</td>
</tr>
<tr>
<td>Disordered c-Si(111) (Ar$^+$ ion bombarded)</td>
<td>0.60</td>
<td>0.13</td>
<td>0.05</td>
<td>0.28</td>
<td>0.55</td>
</tr>
<tr>
<td>Hydrogenated c-Si(111) (H$^+$ ion bombarded)</td>
<td>0.40</td>
<td>0.11</td>
<td>0.17</td>
<td>0.31</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Not only are the UHV surface analysis techniques able to give a semi-quantitative measure of the total amount of hydrogen in a-Si:H samples, they are also able to provide semi-quantitative information about the relative amounts and different types of hydrogen bonding. This can be seen from Figure 6 which shows the L$_{1,2}$V Auger spectra and the areas of the corresponding decoupled components for a-Si:H samples prepared in two different ways. Sample 1 in Figure 6 is an a-Si:H sample prepared by H$^+$ ion implantation of a disordered c-Si sample while sample 2 was prepared by allowing the surface of an Ar$^+$ bombarded a-Si:H sample (prepared by glow discharge) to rehydrogenate for 88 hours.

![Figure 5: Comparison of the decoupled components of the L$_{1,2}$V Auger spectra of Figure 3 for c-Si, a-Si (disordered c-Si) and a-Si:H (disordered and hydrogen ion bombarded c-Si) samples.](image)
Although the two samples have similar total hydrogen contents as shown by similar ratios in the right most column of the table in Figure 6, they have differently shaped $L_1L_2,V$ Auger lines (and therefore VB DOS). By decoupling these lines and measuring the areas of the different component peaks it is possible to see that this is due to different amounts of Si-H, Si-H$_2$ and Si-H$_3$ bonding in the two different samples. The sample prepared by hydrogen ion bombardment of c-Si has more Si-H while the rehydrogenated glow discharge sample has more Si-H$_2$ and Si-H$_3$ type bonding. It is clear from the results and discussion above that the use of the Si $L_1L_2,V$, $L_2,VV$ and XPS VB lines, together with their decoupled components provide a powerful, semi-quantitative method for studying the effects of disorder and hydrogenation in a-Si:H materials produced for solar energy applications.

1.3 The use of UHV Characterisation Techniques to Study Applied Problems in a-Si:H Solar Cell Materials and Devices

One of the most serious impediments to the commercial development of amorphous silicon solar cells is the existence of photodegradation or the Staebler-Wronski effect (SWE) [Nevin et al., 1989; Wakisaka et al., 1992]. This effect was discovered nearly twenty years ago [Staebler and Wronski, 1977] and considerable effort has been devoted to methods of overcoming it, but so far no complete cure has been found [Nevin et al., 1989; Wakisaka et al., 1992]. The SWE manifests itself as a decline in the photovoltaic conversion efficiency of amorphous silicon solar cells with time under illumination [Wronski, 1984]. Typically the PV efficiency falls rapidly during the first few days of exposure to light, followed by a slower, exponential decay which gradually approaches an asymptote over a period of several months. Early samples showed a relative decay in the efficiency of up to 30% but some modern designs have reduced the SWE to around 10% [Zemen and Schropp, 1994; Guha et al., 1996]. Kazmerski [1989] has identified a number of fundamental issues still unresolved in the SWE, including the role of hydrogen, film structure and the nature of defects in the bandgap.

UHV characterisation techniques can be used to study fundamental material properties, but they can also be applied to the study and solution of practical material and device problems such as the SWE. Although there are a number of theories about the cause and mechanism of the SWE [Stutzman, 1985; Eser, 1987, Morigaki, 1988, Clare et al, 1997b] they all involve the breaking of Si-X bonds (where X may be for example Si or H) leading to an increase in the number of dangling bonds in the lattice and therefore the number of $p$-like states at the top of the VB. It is also known that the way in which the Si and H are bonded in the a-Si:H affects the amount of degradation. Films that contain more Si-H$_2$ and Si-H$_3$ bonds are more susceptible to the SWE. It is also accepted that annealing in the dark leads to the broken bonds being passivated by hydrogen in the lattice [Stutzman, 1985; Eser, 1987; Morigaki, 1988]. We have shown above that changes in the VB DOS due to disorder, hydrogenation and the different types of Si-H bonding can be clearly monitored both qualitatively and semi-quantitatively using the UHV characterisation techniques described. Therefore these techniques are promising tools to study some of the unresolved issues of the SWE as well as other practical device fabrication and operational problems.
Srinivasan and colleagues [Srinivasan et al., 1988, 1989; Srinivasan, 1990; Srinivasan and Nigavekar, 1989] have used the Si $L_{2,3}VV$ and XPS VB lines to study a number of fundamental properties of a-Si:H solar cell devices as well as more applied problems. These include the role of dopants in the electronic structure of a-Si:H [Srinivasan and Nigavekar, 1991], thermal equilibrium in a-Si:H [Srinivasan, 1990], metastability and microstructural changes in a-Si:H [Srinivasan et al., 1988] and illumination-induced reversible changes in the valence band densities of states of a-Si:H [Srinivasan et al., 1989]. We also plan to apply these UHV characterisation techniques to study the effects of annealing and the SWE on a-Si:H materials prepared for solar cell devices.

2 CONCLUSIONS

We have discussed how:

- UHV characterisation techniques can be used to gain a wide variety of information about device quality a-Si:H solar cell materials, including chemical information, the nature of the structure and bonding of the material, and the role these factors play in determining device performance and stability.
- Auger and x-ray photoelectron spectroscopy can give a wealth of chemical information about a-Si:H material, including chemical composition and are widely used for material characterisation and device troubleshooting.
- These UHV characterisation techniques not only give information on the elemental composition and chemical environment of a-Si:H but can also give valuable structural and bonding information. Analysis of the lineshapes of the Si $L_{2,3}VV$, $L_{1}L_{2,3}V$ and XPS valence band spectra can give a lot of information about changes in the electronic nature of a-Si:H due to disorder, hydrogenation and different types of Si-H bonding in the material.
- The use of the Si $L_{1}L_{2,3}V$, $L_{2,3}VV$ and XPS VB lines, together with their decoupled components provide a powerful, semi-quantitative method for studying the effects of disorder and hydrogenation in a-Si:H materials produced for solar energy applications.
- These UHV characterisation techniques can not only be used to study fundamental material properties but can also be applied to the study of practical material and device problems such as the Staebler-Wronski effect.

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