XPS in-depth composition study on commercial monocrystalline silicon solar cells

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INTRODUCTION

At the end of the manufacturing process of positive doped monocrystalline silicon solar cells, each device is subjected to an efficiency test in order to classify cells of different quality and to exclude those that yield too small photocurrent under standardized conditions for the assembly of the solar panel (ISOFOTON, Malaga, Spain). Furthermore, the quality test permits cells of equal power to be mounted in each solar panel, and therefore to a maximum of the power generated in each panel. Solar panels can be classified according to their output power, and a quality (output power)-dependent price fixing for each panel can be made to make the product more competitive for the market.

Although techniques applied to the manufacture of monocrystalline silicon solar cells have been well established for about two decades, the reason why some cells yield a worse result than others from the same production line is often unknown. A low photocurrent can be due, among other things, to a larger amount of defects or impurities in the silicon bulk, which would increase the recombinations of the charge carriers before their recollection at the electrodes, or simply due to a bad electrical contact of the electrodes to the silicon bulk material. The front contact is usually made with metallic deposits of silver in the form of so-called fingers. After finger screening the silver atoms have to diffuse during the final firing process at 973 °C, through the TiO₂ anti-reflection layer and the SiO₂ passivation layer, up into the phosphorus-doped silicon bulk in order to make the electrical front contact of the solar cell device. A more detailed description of the manufacturing process of the solar cells studied in this work is reported in a previous paper.

In this work, XPS together with argon ion depth profiling is used for compositional and chemical analysis in the required range of depth of the front side of the solar cell device. Both SIMS and secondary neutral mass spectrometry (SNMS) have been applied in the past, in that case to amorphous (a) Si solar cells produced at laboratory level to study impurities at the ZnO/a-Si or SnO₂/a-Si interface. However, to our knowledge, there has not been any study published on monocrystalline solar cell devices of large-scale production using spectroscopic techniques combined with ion etching for depth profiling. In this work, two monocrystalline silicon solar cells, both cut in wafers from the same p-doped silicon monocrystal and fabricated in the same manufacturing line, are compared by XPS depth profiling. They are of very different quality, i.e. yielding in one case a standard short-circuit photocurrent of 3.0 A (good cell) and in the other case a very low value of only 1.6 A (bad cell), both under standardized conditions of illumination. We present for both cells a comparative study of the chemical composition versus depth by profiling through the TiO₂ anti-reflection layer, the SiO₂ passivation layer and up into the phosphorus-doped silicon bulk (emitter). This study has been done on the photovoltaically active part of the solar cell, i.e. far away from the metallic fingers or front contact of the solar cell device. This work is a continuation of investigations with XPS carried out in our laboratory on real solar cell devices manufactured by ISOFOTON (Malaga, Spain).
EXPERIMENTAL

Two monocrystalline silicon solar cells manufactured by ISO-FOTON (Málaga, Spain) have been studied. Monocrystalline p(boron)-doped silicon grown in the (111) direction by the Czochralski method and cut in slices (wafers) 0.30–0.35 mm thick have been used as the source material for solar cell manufacturing. The manufacturing process can be separated roughly into the following successive fabrication steps: surface texturing; phosphorus diffusion; SiO2 passivation layer formation; TiO2 anti-reflection coating and crystallization into the rutile phase by calcination; finger screening and firing of the final device for electrical contact formation. The different surfaces exposed during the manufacturing process have been studied previously.3 Both solar cells under study in this work proceed from the same monocrystal and the same manufacturing series but yield significantly different photocurrents; Isc = 3.0 A (good cell), called SC3.0; and Isc = 1.6 A (bad cell), called SC1.6. This difference in photocurrent means a difference in output power of ~50%.

The XPS measurements were carried out on a PHI 5700 spectrometer with an argon ion gun coupled to the main chamber. Multi-region spectra were recorded from a 380 µm diameter analysis area at 45° take-off angle with a concentric hemispherical energy electron analyser operating in constant pass energy mode at 29.35 eV, using Mg Kα radiation (1253.6 eV) as the excitation source at a power of 300 W (15 keV). Under these conditions, the Au 4f7/2 line was recorded with 1.16 eV full width at half-maximum (FWHM) at a binding energy of 84.0 eV. The spectrometer energy scale was calibrated using Cu 2p3/2, Ag 3d3/2 and Au 4f7/2 photoelectron lines at 922.7, 368.3 and 84.0 eV, respectively. The pressure in the analysis chamber was lower than ~10⁻⁷ Pa and during 4 keV Ar⁺ depth profiling it was ~10⁻⁵ Pa. The argon ion gun was at an angle of 50° with respect to the sample surface. The sputtered sample area was 4 × 4 mm² in order to be sure that the analysed area during depth profiling is sputtered uniformly and hence at equal depth at a given sputter time. A sputter rate of 1.2 nm min⁻¹ has been determined for a 100 nm thick Ta2O5 film, yielding a depth resolution of ~10 nm for the Ta2O5/Ta interface.

Two types of depth profiles have been performed:

(1) Sequence programmed profiling: sequences of 2 min sputter time, 2 s delay time (to reduce 4 keV Ar⁺ sputter-induced sample charging) and thereafter recording of the multi-region spectra of elements in major concentrations (titanium, oxygen, silicon) by only a few sweeps over each recording region (Ti 2p, O 1s and Si 2p) up to a total sputter time equivalent to a certain number of sputter sequences.

(2) Manual profiling: sputtering for a certain time (sequence) up to the desired depth, closing (after each sputter sequence) the argon gas inlet and thus lowering the pressure to ~10⁻⁷ Pa before recording the multi-region spectra for a sufficiently long time to be able to detect elements in minor concentration.

In this way, C 1s, Ag 3d, Pb 4f and P 2p besides Ti 2p, O 1s and Si 2p photoelectron peaks have been recorded after each sputter sequence. Detection limits of ~0.2 at.% for carbon and 0.05 at.% for silver have been achieved. The PHI ACCESS ESCA-V6.0 F software package was used for data acquisition and analysis. The atomic concentrations were calculated from the photoelectron peak areas using Shirley background subtraction and sensitivity factors provided by the spectrometer manufacturer (PHI, Eden Prairie, MN, USA).

The morphological aspect of both solar cells has been studied with a JOEL JMS 6300 electron microscope working at 10 keV. For this, both samples have been covered with a thin gold film to prevent any charging during electron bombardment. Reflectivity measurements were carried out with a Shimadzu UV-VIS-nIR spectrometer with integrating sphere to evaluate the reflectance of both solar cells.

RESULTS AND DISCUSSION

The SEM pictures of the surfaces of both samples are shown in Fig. 1. It can be seen that the wafer surface of SC3.0 presents pyramids of more or less uniform size, whereas that of SC1.6 shows pyramids of varying size between 1 and 10 µm approximately. These pyramids have been formed by chemical etching (texturing) of the Si(100) wafer surface. They are of quadratic base with four Si(111) faces. Figure 1 reveals that the etching process has not been equally efficient for both surfaces, although both wafers have passed the
same humid acid line for texturing in the manufacturing process. Texturing of the p-Si wafer surface increases the photovoltaic active surface by ~25–30%. Hence there must be further reasons that explain the large difference (nearly 50%) measured in efficiency of both solar cells.

In order to evaluate the influence of the different texturing, we measured the reflectance of both solar cell surfaces. This is shown in Fig. 2 together with the global solar spectrum AM 1.5. Little difference in the reflectance spectra of both solar cells is observed in spite of the very different pyramid size revealed by SEM. The mean solar absorption coefficient has been determined for both cells:

\[ \alpha_{\text{solar}}(\text{SC3.0}) = 0.833 \]
\[ \alpha_{\text{solar}}(\text{SC1.6}) = 0.826. \]

Hence, the optical data cannot explain the strong difference observed in the photocurrent.

In Fig. 3 the relative atomic concentrations of titanium, oxygen and silicon versus 4 keV Ar⁺ sputter time (sequence programmed profiling, see Experimental) are shown for both solar cells. In both depth profiles for about the first 25 min of sputtering, we detect titanium and oxygen atoms according to the TiO₂ anti-reflection layer. Then the titanium concentration drops but the silicon concentration increases and the oxygen concentration stays constant due to profiling in the SiO₂ passivation layer. Finally, the oxygen concentration drops to zero and only silicon is detected when reaching the silicon bulk of the solar cells. During 4 keV Ar⁺ sputter profiling, the atomic concentrations measured do not necessarily reproduce the stoichiometric composition of the layers. This is due to preferential sputter removal of some elements, as occurs in TiO₂, for instance, where oxygen is sputtered preferentially.

In Table 1 for both solar cells we present the layer thickness in minutes of 4 keV Ar⁺ sputter time determined from the depth profiles of Fig. 3. In parentheses are given the estimated thickness values by taking into account the sputter yield in TiO₂ and SiO₂ relative to Ta₂O₅ at 4 keV Ar⁺ bombardment. Comparing both solar cells, the differences in layer thickness are much smaller than the depth resolution determined from the profiles. As can be seen in Fig. 3, the depth resolution has worsened considerably compared to that determined for the Ta₂O₅/Ta interface when calibrating the 4 keV Ar⁺ sputter rate. It has been found to be roughly 25 min of 4 keV Ar⁺ sputtering for the TiO₂/SiO₂ interface and 50 min of 4 keV Ar⁺ sputtering for the SiO₂/Si interface. This is due mainly to the high surface roughness of the textured wafers. In our case with a very complex surface geometry, even rotation of the samples during 4 keV Ar⁺ texturing, we measured the reflectance of both solar cell surfaces.

The poor depth resolution due to the surface morphology of our samples is the reason why no differences can be observed in the depth profiles of sequence programmed profiling. However, these profiles of Fig. 3 permit us to

![Figure 2. Absolute reflectances of SC3.0 and SC1.6. The global solar spectrum AM1.5 is also shown. Mean solar absorption coefficients for both cells are indicated.](image1)

![Figure 3. Titanium, oxygen and silicon depth profiles from sequence programmed profiling (see Experimental) for SC3.0 (top) and SC1.6 (bottom).](image2)

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO₂</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC3.0</td>
<td>34 (47)</td>
<td>63 (64)</td>
</tr>
<tr>
<td>SC1.6</td>
<td>32 (44)</td>
<td>65 (66)</td>
</tr>
</tbody>
</table>

Values in parentheses are estimated layer thicknesses in nanometres by taking into account Ta₂O₅ relative sputtering yields (a sputter rate of 1.2 nm min⁻¹ has been determined in Ta₂O₅).
determine the sputter time (depth) necessary to reach the different layers and interfaces in both solar cells and thus make it possible to sputter to a certain depth of interest and record multi-region spectra at ultrahigh vacuum (better than \(10^{-7}\) Pa) with sufficient recording time for each photoelectron peak to allow the detection of elements in minor concentrations. Such elements are phosphorus, lead, silver and carbon. These elements have been found in a previous study as traces at the photovoltaically active part of the solar cell surface.\(^1\) The distribution at the surface and versus depth of these elements is decisive for the efficiency of the solar cell device: phosphorus is the element that makes the p-n junction in the p-doped silicon bulk; silver has to diffuse through the surface layer system into the silicon bulk, but not passing the p-n junction (because it would make a short-circuit), in order to make a good electrical front contact; carbon is isovalent to silicon and has a smaller atomic radius so that it can diffuse easily into the silicon bulk and act as a recombination centre for charge carriers; lead atoms can act as dispersion centres for light absorption, thus reducing the light transmission into the silicon bulk for electron–hole pair generation.

Table 2 shows the atomic concentrations determined for the surfaces of both solar cells, i.e. before 4 keV Ar\(^+\) sputter profiling. As can be seen, relatively large amounts of the elements in minor concentration (i.e. carbon, phosphorus, silver and lead) have been found at the surfaces. In Table 2 one can observe that at the surface of SC1.6 (bad cell) a larger amount of carbon, lead and phosphorus has been found than at the surface of SC3.0. Amounts of phosphorus at the top surface of the solar cell device (TiO\(_2\) anti-reflection layer) indicate a redistribution of this element through the layer system during the thermal processes of manufacturing, as has been shown in a previous study.\(^3\) Besides, it could also affect the depth of the p-n junction in the solar cell device. Furthermore, a large amount of carbon and lead at the surface leads to a reduction of transmitted light into the region of the p-n junction.

On the other hand, manual depth profiling (see Experimental) has shown that lead and phosphorus concentrations decrease below the XPS detection limit (~0.1%) in ~8–10 min of 4 keV Ar\(^+\) due to preferential sputtering of these elements. However, carbon and silver concentrations could be followed for both solar cells, profiling through the layers up into the silicon bulk. The corresponding atomic concentrations of silver and carbon determined from the Ag 3d and the C 1s photoelectron peaks are shown versus 4 keV Ar\(^+\) sputter time in Fig. 4. In the lower part of the figure the carbon concentration is presented in an expanded scale to show the differences between both cells. In the top part we can see that the silver concentration drops for SC1.6 in ~30 min below the XPS detection limit, whereas for SC3.0 it drops within the first few minutes but then stays at detectable concentrations of ~0.1–0.2 at.% until deep into the silicon bulk. This shows that in SC1.6 silver is present, at least at this local site of the solar cell where the depth profile study has been performed, in the zones of the anti-reflection (TiO\(_2\)) and the passivation (SiO\(_2\)) layers but not in the silicon bulk. Hence, in comparison to SC3.0, where silver is present up into the silicon bulk, we can deduce that silver atoms have not diffused sufficiently in SC1.6 to make a good electrical contact. On the other hand, the carbon concentration decreases drastically in only 1 min of 4 keV Ar\(^+\) sputtering, due to adventitious carbon at the sample surfaces, and then carbon stays at a detectable level in the whole depth range studied. We can see in Fig. 4 (bottom, expanded atomic concentration scale) that the carbon concentration is always higher in the TiO\(_2\) layer than in the SiO\(_2\) layer or the silicon bulk, and it is always higher in SC1.6 than in SC3.0. The latter finding of a greater amount of carbon at all the studied depths in SC1.6 indicates a larger amount of impurities, which are known to act as centres for charge carrier recombination.\(^2\)

**CONCLUSIONS**

The comparison of a solar cell of good quality (high photocurrent of 3.0 A) with one of bad quality (low photocurrent of only 1.6 A) has shown that all manufacturing processes are decisive for the final quality of the solar cell device. For the solar cell of bad quality (SC1.6), it was...
found that the surface texturing is more irregular and the amounts of impurities (carbon, phosphorus and lead) in the uppermost atomic layers are distinguishably higher. Furthermore, silver atoms have not diffused sufficiently in SC1.6 from the top surface into the silicon bulk to make a good electrical front contact of the solar cell device.

Acknowledgement
The financial support of the Junta de Andalucía (Spain) through research group FQM192 is gratefully acknowledged.

REFERENCES