

RESEARCH ARTICLE

Depth Profile Analysis of Amorphous Silicon Thin Film Solar Cells by Pulsed Radiofrequency Glow Discharge Time of Flight Mass Spectrometry

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GD-TOFMS

Abstract. Among the different solar cell technologies, amorphous silicon (a-Si:H) thin film solar cells (TFSCs) are today very promising and, so, TFSCs analytical characterization for quality control issues is increasingly demanding. In this line, depth profile analysis of a-Si:H TFSCs on steel substrate has been investigated by using pulsed radiofrequency glow discharge-time of flight mass spectrometry (rf-PGD-TOFMS). First, to discriminate potential polyatomic interferences for several analytes (e.g., ²⁸Si⁺, ³¹P⁺, and ¹⁶O⁺) appropriate time positions along the GD pulse profile were selected. A multi-matrix calibration approach, using homogeneous certified reference materials without hydrogen as well as coated laboratory-made standards containing hydrogen, was employed for the methodological calibration. Different

calibration strategies (in terms of time interval selection on the pulse profile within the afterglow region) have been compared, searching for optimal calibration graphs correlation. Results showed that reliable and fast quantitative depth profile analysis of a-Si:H TFSCs by rf-PGD-TOFMS can be achieved. **Keywords:** Pulsed glow discharge, Time of flight mass spectrometry, Multimatrix calibration, Depth profiling, Amorphous silicon thin film solar cells

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Introduction

D uring the last years, the use of solar cells has grown considerably because of their increasingly improved practical characteristics (cost, size, performance, etc.). Despite the fact that crystalline silicon solar cells dominate the market today [1], thin film solar cells (TFSCs) based on hydrogenated amorphous silicon (a-Si:H) also constitute a promising alternative technology [2, 3]. TFSCs analytical characterization is a very important issue to guarantee the required performance and quality. For routine purposes, optical and electrical properties are commonly just measured. How-

ever, elemental depth profiling characterization is also important to investigate the thickness of the layers, the presence of interdiffusion processes, as well as the extent of unwanted impurities.

Among the different direct solid analysis techniques, glow discharge (GD)-based instruments are very appropriate for the characterization of thin layered samples because of their good depth resolution (few nanometers), low matrix effects, and high sample throughput (less than 5 min per analysis) [4, 5]. A GD plasma is initiated when applying a high potential (~kV) between two electrodes containing a discharge gas (e.g., Ar). The discharge gas is electrically broken down to form electrons and positive ions, which are accelerated towards the cathode surface (the sample). Release of cathode material into the gas phase (sputtering process) is achieved attributable to the bombardment of the cathode by positive ions and fast atoms with sufficient energy. The use of radiofrequency (rf) to powering the GDs extends the direct analysis to nonconducting materials [6]. Moreover, the application of pulses to the GDs gives rise to

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higher analytical sensitivity [7], while reducing the thermal stress in the analyzed samples [4]. In pulsed mode, the plasma is a dynamic system as the discharge is switched on and off periodically, thus producing different ionization mechanisms during the pulse period. The maximum sensitivity can be found in the afterglow region, some microseconds after the pulse is off. In general, monoatomic ions are formed in the first microseconds of the afterglow region and polyatomic ions are formed afterwards due to ion recombination.

Typical detection systems for GDs are optical emission spectrometry (OES) and mass spectrometry (MS). In particular, the use of pulsed GD (PGD) in combination with time of flight mass spectrometry (TOFMS) has proven to be a recent promising approach for the analysis of thin layers [8]. In this vein, it has to be highlighted that the combination of a PGD (generating a dynamic plasma) to TOFMS (fast enough to collect data at different time intervals during the pulse) can allow the reduction or even removal of spectral interferences by integrating a proper pulse interval [7, 9]. Spectral interferences removal is crucial for the quantification of some important analytes, such as ${}^{28}\text{Si}^+$, which could be interfered by ${}^{12}\text{C}{}^{16}\text{O}^+$ and ${}^{14}(\text{N})_2^+$.

In the last years, rf-PGD-TOFMS has been successfully tested and applied for the analysis of rather varied materials, such as polymers [10], ultra-low energy implants [11], fluorine-containing tantala layers [12], or even isotopically enriched pellets [13]. Concerning GD applications to photovoltaic materials, GD-OES and GD-MS have been employed, for example, for the analysis of aluminium doped ZnO films [14], boron implanted and solar grade silicon [15, 16]. In particular, rf-PGD-OES has been recently investigated in our group for depth profiling analysis of a-Si:H TFSCs [17]. In this context, it should be stressed that the presence of hydrogen in a-Si:H thin films could represent a challenge for quantitative analysis because of the so-called "hydrogen effect": it has been previously reported that the addition of hydrogen to Ar GD could affect the intensity of the analytes and reduces the sputtering rate [18, 19]. We have reported that molecular hydrogen added to the discharge gas seems to play a more critical role than the endogenous hydrogen present in the sample itself (e.g., for samples with hydrogen content in the order of 10% atomic) [20, 21].

In this manuscript, quantitative depth profiling analysis of a-Si:H TFSCs has been investigated for the first time by using rf-PGD-TOFMS. A multi-matrix calibration approach using homogeneous certified reference materials (CRMs) without hydrogen as well as coated laboratory standards with hydrogen were employed for silicon, boron, and phosphorous calibrations. Different time positions along the pulse profile were investigated in order to reduce polyatomic interferences for several analytes (e.g., ²⁸Si⁺, ¹¹B⁺, ³¹P⁺, and ¹⁶O⁺). Additionally, several calibration strategies were studied, using different integrations along the pulse profile afterpeak region.

Experimental

Samples Preparation: TFSCs Based on a-Si:H

TFSCs based on hydrogenated amorphous silicon were prepared using 4.5 cm diameter and 1.6 mm thick mirror polished stainless steel ($0.017\pm0.001 \mu$ m average roughness and $0.14 \pm0.03 \mu$ m maximum peak-to-valley roughness). Such photovoltaic devices consist of the following stack (from back to front): stainless steel substrate // Al (280±10 nm) // Al-doped zinc oxide (AZO) (270±10 nm) // n-a-Si:H/intrinsic a-Si:H/p-a-SiC:H (420±21 nm) //AZO (480±15 nm).

The Al layer was deposited by thermal evaporation (Model Classic 500; Pfeiffer, Asslar, Germany) using Al dust with a purity of 99.999%. The AZO layer was sputtered from ceramic ZnO:Al₂O₃ (2 wt%) target by using a magnetron sputtering-up physical vapor deposition (PVD) system (ATC Orion 8HV; AJA International, Boston, Massachusetts, USA) at room temperature an applying a rf power and pressure of 120 W and 2.2 mTorr, respectively. The amorphous silicon layers were deposited by conventional plasma enhanced chemical vapor deposition (PECVD) in a cluster configuration system (Elettrorava, Model V0714, Torino, Italy), which has three separate process chambers for the deposition of intrinsic, n-type and p-type layers in order to avoid cross-contamination. Deposition processes were carried out with a rf forward power of 1.8 W, a fix frequency of 13.56 MHz, and the heating system temperature and pressure during deposition varied from 260 to 210°C and 500 to 900 mTorr, respectively (depending on the layers). Concerning the gas reaction processes, the p-a-SiC:H layer was deposited by mixing SiH₄ (10 sccm), B_2H_6 (12 sccm), H_2 (15 sccm), and CH_4 (10 sccm), the n-a-Si:H layer by mixing SiH₄ (6 sccm), H₂ (30 sccm), and PH₃ (4 sccm), and SiH₄ (20 sccm) was used for the intrinsic a-Si:H layer growth. The different gases were delivered by Praxair (Madrid, Spain). The layer thicknesses were determined on cross-sectioned witness samples by using a mechanical step profilometer (Model XP-1, Ambios technology, Santa Cruz, California, USA).

Additionally, individual p-a-SiC:H and n-a-Si:H layers were prepared on stainless steel substrate for optimization of GD experimental conditions and for investigating different time positions along the pulse profile for the accurate measurement of analytes. For the synthesis of these samples, the same gas flow rates as those used for the complete TFSCs were employed just varying the deposition times.

Standard Materials and Calibration Procedure

Multi-matrix calibrations for the quantification of rf-PGD-TOFMS profiles were carried out using 22 bulk CRMs. Standards based on different matrices, including Fe, Ni, Ti, Al, Zn, Si, and Cu, as well as wide ranges of analyte mass fractions were used in the calibration curves: elemental concentrations varied from few μ g/g up to high percentages (e.g., 95% Zn, 93% Fe, 86% Al, etc.). Before the analysis by rf-PGD-TOFMS, CRMs were polished using metallographic grinding papers (SiC: 220, 800, and 1200 grit) and afterwards cleaned with ethanol to avoid contamination traces. The shape and depth of the craters were measured by mechanical profilometry. Two profile traces in different directions across the center of each crater were measured in all cases. Sputtering rates, evaluated as mass loss per unit time during the sputtering, were calculated by measuring the penetration depths per unit time and considering the crater diameter and material density. The mean of three sputtered replicates was always used.

TFSC based on a-Si:H have an important hydrogen content (up to 11 at%). However, the availability of CRMs containing hydrogen is still scarce and, when hydrogen is present, its concentration is low. Therefore, laboratory standards were prepared for hydrogen quantification in a-Si:H TFSC. The synthesis of hydrogen standards was performed by deposition of intrinsic a-Si:H layers onto a stainless steel substrate using different temperatures, from 200 to 400°C. All the experiments were carried out in the PECVD equipment applying a SiH₄ flow rate of 20 sccm until a-Si:H layers with a thickness in the range of 400-500±15 nm was achieved. The hydrogen content was then calculated by using Fourier transform infrared spectroscopy (FTIR). IR-absorption measurements between 2800 and 400 cm⁻¹ wavenumbers using a FTIR Nicolet 6700 spectrometer (Thermo Scientific, Waltham, Massachusetts, USA) in transmittance mode were performed under inert atmosphere. A verification of the equipment was first carried out by means of a mid-IR wavelength standard and accuracy below 5% was found. Then, a background spectrum, using a microelectronic quality Si wafers substrate was carried out. Hydrogen contents achieved for three hydrogen laboratory standards were found to be in the range between 8% and 13% (at%).

Only few CRMs were available in our lab for boron and phosphorous calibration. Moreover, such standards did not contain hydrogen, as it is the case of boron and phosphorous doped layers (n-a-Si:H and p-a-SiC:H) on the complete TFSC. Thus, several individual p-a-SiC:H and n-a-Si:H layers were grown on stainless steel to prepare laboratory standards for B and P calibrations. Individual p-a-SiC:H and n-a-Si:H layers were grown by PECVD using different B₂H₆ and PH₃ flow rates. In these cases, the process temperature and layer thickness were kept constant at 280°C and 400±18 nm, respectively. The boron and phosphorous contents were then calculated by using inductively coupled plasma (ICP), either coupled to optical emission or to mass spectrometry (ICP-OES for P analysis and ICP-MS for B analysis). A quadrupole ICP-MS from Agilent Technologies, Santa Clara, California, USA (7500 ce) and an ICP-OES from Varian, Palo Alto, California, USA (Model Vista Pro) were used for the measurements after dissolving the samples using HF:HNO₃ (7:1) for B determination and HF:HNO3:H2SO4 for P determination. Boron- and phosphorous-containing standards with concentrations in the range of 0%-2.7% and 0%-9.1%, respectively, were employed for calibration of p-a-SiC:H and n-a-Si:H layers.

It is typically established that analyte ion signal depends upon two rather independent factors in GD sources: the sputtering rate (density of analyte atoms in the plasma) and the ionization efficiency of those atoms (ionization yield). The basic calibration function most commonly used in GDs is of the following form:

$$I_i = R_i q_M C_i + b_i$$

where I_i is the ion intensity of isotope measured of element i, R_i is the ionization yield, q_M is the sputtering rate of the certified reference materials used for calibration (in mass per unit area per second), C_i is the concentration of element i, and b_i is the background signal. The ionization yield is an atom- and instrument-dependent parameter, which must be determined independently for each ion and instrument. The approaches developed so far to obtain quantitative compositional depth profiling are based on the assumption that the ionization yield in GDs is essentially a matrix-independent quantity. Thus, calibration curves employed for quantification of multilayered samples by GD sources are in the form of ion signals versus the product of concentration and sputtering rate.

Instrumentation

A rf-PGD-TOFMS prototype was used for the experiments. It has a rf-PGD bay unit (provided with a pulsed rf generator, matching box, rf-connector, and a mounting system with a pneumatic piston to press the sample against the GD) supplied by Horiba Jobin Yvon (Longjumeau, France). The rf-PGD source is coupled to an orthogonal time-of-flight mass spectrometer (TOFWERK, Switzerland) with a microchannel plate detector [22]. This coupling was performed with a 0.5 mm orifice diameter sampler and a 1.0 mm orifice diameter skimmer, with a separation of 7 mm between them.

The GD source can work in pulsed mode, generating pulses with a pulse period from 0.1 ms up to 100 ms and pulse width from 50 μ s up to several ms. The radiofrequency generator operates at 13.56 MHz. The power is supplied from the back side of the sample and a refrigerating disc is used to keep the samples at temperatures lower than 6°C. In our case, 2 ms of pulse width and 4 ms of pulse period have been selected for the measurements. The time-of-flight mass spectrometer was operated with an ion extraction rate of 33 μ s/extraction (there are 33 μ s between the start of an ion extraction and the start of the following one). In order to motorize the beginning of the pulse, a 150 ns delay was employed to ensure a complete acquisition of MS signals between GD pulses. Further details of GD-MS instrument can be found in previous work [7].

A GD chamber (supplied with the device) was used for this work. The GD chamber is made of copper and its design is similar to those used in the commercial GD-OES instruments from Horiba Jobin Yvon, with a 4 mm diameter anode and 15.5 mm thickness. A flow tube with 2.5 mm inner diameter is inserted from the back of the anode to face the gas flow towards the cathode surface [23]. Such discharge chamber is compatible with an argon pre-chamber that has been used in our experiments [10, 24]. Ar pre-chamber is filled with argon and isolates the GD discharge chamber from external air, preventing microleaks that could be the source of polyatomic ions that may interfere with some analytes. The procedure for this 'argon

bath' consists of directing an argon flow towards the discharge chamber some seconds before putting the sample in the chamber. The argon displaces the air, thus reducing air species in the discharge chamber. These air species are further reduced by waiting 15 min before the measurement, while the vacuum pumps remove the remaining air.

Results and Discussion

The optimization of Ar pressure and rf forward power was carried out in preliminary studies to obtain the best depth resolution, while maximizing sensitivity, using individual p-a-SiC:H and n-a-Si:H layers deposited on stainless steel. The optimum conditions were 600 Pa and 90 W, similar to previous experiments [21]. As expected [7, 22], higher analytical signals were obtained in the afterpeak region of the pulse profile, and so the afterpeak will be the only temporal region in the GD pulses shown throughout this Results and Discussion section.

Interference Removal Studies

As previously mentioned, PGDs in combination with TOFMS can allow the reduction or even removal of spectral interferences by selecting and integrating a proper GD pulse interval. For the analysis of TFSCs, analytes such as phosphorus and silicon are susceptible to be affected by polyatomic interferences. Thus, different time delays along the pulse time profile were investigated for several isotopes of interest in these samples in order to obtain accurate results. Possible spectral interferences in phosphorus detection were first studied. Phosphorus has only one isotope (^{31}P) , which can be interfered by the presence of ${}^{14}N^{16}O^{1}H^{+}$ and ${}^{30}Si^{1}H^{+}$. The pulse profile of ³¹P⁺, observed in the afterpeak region for the analysis of an individual n-a-Si:H laver deposited on stainless steel, is shown in Figure 1a. As can be seen, the pulse profile presents two peaks, the first one being more intense (the second peak shows up just as a shoulder). As collected in Figure 1b, the ${}^{14}N^{16}O^{1}H^{+}$ signal did not appear in the mass spectra when selecting the maximum position of the afterpeak region for data treatment, but it becomes visible when data were taken at longer times in the afterpeak (Figure 1c). Therefore, the maximum of the afterpeak was chosen as the optimum region for phosphorus determination. Regarding ³⁰Si¹H⁺, a mass resolution close to 4000 should be required to discriminate ${}^{31}P^+$ and ${}^{30}Si^{1}H^+$. We have measured amorphous silicon layers without phosphorus in order to evaluate such interference. Although not shown in the manuscript, one peak was found coincident with ³¹P⁺ for



Figure 1. Analysis of n-a-Si:H individual layer deposited on stainless steel (5.8% P). (a) ${}^{31}P^+$ pulse profile in the afterpeak region; (b) mass spectrum at m/z 31 selecting the afterpeak maximum position in the pulse profile (position 1 in Figure 2a); and (c) mass spectrum at m/z 31 selecting a later interval in the pulse profile (position 2 in Figure 2a)

that sample in the mass spectrum (when measuring in the maximum of the afterpeak region in the GD pulse profile) whose intensity was slightly higher than the background signal. Such peak could be attributed to trace concentrations of P in the sample or to the ${}^{30}\text{Si}{}^{1}\text{H}^{+}$ interference, which could not be distinguished. Considering the sensitivity of our rf-PGD-TOFMS for P, such signal corresponds to around 80 ppm of P (so, rather close to the expected P detection limit).

Concerning boron dopant, this element has two isotopes: ¹⁰B (isotopic abundance: 19.9%) and ¹¹B (isotopic abundance: 80.1%). As shown in Figure 2a, both isotopes exhibited similar pulse profiles with two maxima in the afterpeak region, the second one being slightly higher. However, the experimental ¹⁰B/¹¹B isotope ratio showed values below the theoretical isotopic abundance ratio (marked as a horizontal dashed line in the plot), suggesting the possible formation of ¹⁰B¹H⁺. In this case, the laboratory standard used for the experiment not only contains boron but also hydrogen, so the formation of ¹⁰B¹H⁺ polyatomic ion could be attributed to the presence of hydrogen in the sample. To investigate this possibility, boron

calibration curves for ¹⁰B⁺ and ¹¹B⁺ were performed using both CRMs without hydrogen and laboratory standards with hydrogen. Figure 2b and c show, respectively, the ¹¹B⁺ and ¹⁰B⁺ calibration curves obtained by rf-PGD-TOFMS, selecting for measurement the earlier maximum in the afterpeak region. For ¹¹B⁺ calibration (Figure 2b), laboratory standards containing hydrogen showed higher signals than those expected compared with CRMs without hydrogen. Therefore, in contrast to phosphorus, it was not possible to select an optimum interval in the afterpeak region able to completely remove polyatomic interference for ¹¹B⁺. However, such hydrogen-containing standards showed the expected signal intensities for ¹⁰B⁺, and a linear calibration curve with a good correlation coefficient was obtained (Figure 2c).

The pulse profile and mass spectrum of ${}^{16}O^+$ were also investigated in detail. The most significant isotope of oxygen is ${}^{16}O$ (99.76% isotopic abundance) and it can be interfered by ${}^{14}N^{1}H_{2}^{-+}$. The ${}^{16}O^+$ pulse profile (Figure 3a) showed again two peaks in the afterglow region, the first peak being the most intense. As we observed previously for phosphorus,



Figure 2. Analysis of boron. (a) ¹⁰B⁺ and ¹¹B⁺ pulse profiles and ¹⁰B/¹¹B isotope ratio in the afterpeak region for the analysis of p-a-Si:H laboratory standard (1.4% B); (b) ¹¹B⁺ calibration curve obtained by rf-PGD-TOFMS using CRMs without hydrogen (diamonds) and laboratory standards with hydrogen (squares). The first maximum in the afterpeak region (Figure 3a) was selected for data treatment; and (c) ¹⁰B⁺ calibration curve obtained by rf-PGD-TOFMS using CRMs without hydrogen (diamonds) and laboratory standards with hydrogen (squares). The first maximum in the afterpeak region (Figure 3a) was selected for data treatment; and (c) ¹⁰B⁺ calibration curve obtained by rf-PGD-TOFMS using CRMs without hydrogen (diamonds) and laboratory standards with hydrogen (squares). The first maximum in the afterpeak region (Figure 3a) was selected for data treatment



Figure 3. Analysis of CRM CC650A (32% oxygen). (a) ${}^{16}O^+$ pulse profile in the afterpeak region; (b) mass spectrum at m/z 16 selecting the afterpeak maximum position in the pulse profile (position 1 in Figure 4a); and (c) mass spectrum at m/z 16 selecting a later interval in the pulse profile (position 2 in Figure 4b)

polyatomic interferences can be easily removed by selecting the correct interval in the pulse profile. Figure 3b shows the mass spectrum at m/z 16 obtained by selecting the first afterpeak maximum position in the pulse profile. In this case, ${}^{16}O^+$ can be measured without polyatomic interferences. In contrast, as shown in Figure 3c, ${}^{16}O^+$ cannot be accurately measured without interference from ${}^{14}N^{1}H_{2}^{+}$ if the second peak in the pulse profile of Figure 3a was used for the measurement.

Here, it should be stated that some differences can be observed for the maximum position of the afterpeak in the pulse profiles depending on the isotope measured (e.g., Figure 2a and Figure 3a). It has been previously shown that maximum signals for sputtered analytes are obtained in the afterglow region. However, the maximum and the shape of the analytical signal depend on the element [23]. On the other hand, although polyatomics attributable to recombination processes in the GD dynamic plasma are typically produced at the end of the afterglow region, the exact shape depends on the particular polyatomic. Finally, for silicon measurement similar results to those previously reported in experimental works carried out in our group were found [7, 21]. Although several polyatomic interferences can occur for the three Si isotopes (e.g., ¹²C¹⁶O⁺, ${}^{14}N_2{}^{1}H^+$, and/or ${}^{14}N{}^{16}O^+$, respectively), the correct selection of the temporal region in the pulse profile allows measurement

of Si isotopes with greatly reduced interferences. Under the selected GD experimental conditions, the isotopic ratio ${}^{28}\text{Si}^+/{}^{29}\text{Si}^+$ was 18.1, which corresponds to an 8% deviation from the natural isotope abundance ratios.

Qualitative Depth Profile Analysis of TFSCs

Figure 4 shows the qualitative depth profile (signal intensity versus sputtering time) obtained for the a-Si:H TFSC, after selecting for each isotope the previously optimized position in the pulse profile for integration. As can be seen, it was possible to discriminate the different parts of the TFSC: the first AZO layer, the a-Si:H layers (where we can distinguish between the B doped, the intrinsic a-Si:H, and the P doped films), the second AZO layer, the back Al contact layer, and, finally, the substrate. Moreover, oxygen and hydrogen were found to be present in the AZO and a-Si:H layers of the sample, respectively. It should be noted that as already reported for GD sources, deeper layer interfaces appeared slightly less defined than more superficial layers. Also, it is interesting to highlight that the analysis time necessary to analyze the different coating layers was below 40 s, proving that rf-PGD-TOFMS offers an excellent tool for the fast and direct quality control of TFSC production.



Figure 4. Qualitative depth profile (signal intensity versus sputtering time) obtained by rf-PGD-TOFMS for an a-Si:H TFSC deposited on a stainless steel substrate

Evaluation of Hydrogen Effect and Calibration Strategies in rf-PGD-TOFMS

Appropriate calibration graphs must be constructed for all the elements present in the samples in order to convert the qualitative depth profiles obtained by rf-PGD-TOFMS into quantitative depth profiles (mass content versus depth). A multimatrix calibration approach [25] using homogeneous CRMs as well as coated standards has been attempted here. Laboratory standards based on intrinsic a-Si:H layers and individual pa-SiC:H and n-a-Si:H layers (see Experimental section) were employed, together with bulk CRMs for silicon, hydrogen, boron, and phosphorous calibration. Calibration graphs by rfPGD-TOFMS were obtained plotting the net intensity signals versus the product of the mass content of each element in the standard times the measured sputtering rate of the corresponding standard (in μ g/s).

Table 1 shows the fitting parameters obtained for phosphorus and silicon calibration graphs, using both CRMs without hydrogen and laboratory standards containing hydrogen. Additionally, the boron calibration graph using standards with and without hydrogen can be also seen in Figure 2c. It has been reported that the addition of molecular hydrogen to Ar GD affects the intensity of the analytes and, therefore, a different trend for the two types of calibration standard could be expected [26]. However, as previously demonstrated, the endogenous

Table 1. Summary of the Fitting Parameters (Slope, Intercept, and Correlation Coefficients) Found for ³¹P, ²⁸Si, and ⁶⁸Zn Calibration Curves by rf-PGD-TOFMS

Analyte	Data treatment	Calibration curves - Fitting parameters		
		Slope	Intercept	Correlation coefficient
³¹ P	Afterpeak maximum	7493.6	31.5	0.949
²⁸ Si	Afterpeak maximum	7352.2	20.1	0.935
⁶⁸ Zn	Average signal of the whole afterpeak	860.3	22.7	0.999
⁶⁸ Zn	Average signal of the first peak	1505.3	19.5	0.999
⁶⁸ Zn	Average signal of the second peak	696.3	41.6	0.995
⁶⁸ Zn	Signal at the maximum position of the first peak	2115.3	117.6	0.990
⁶⁸ Zn	Signal at the maximum position of the second peak	1032.1	74.1	0.981

hydrogen (a-Si:H layers) does not seem to exhibit such critical influence on ion signal intensities as exogenous hydrogen [21]. As can be seen in Figure 2c and Table 1, a good correlation was obtained for boron, phosphorus, and silicon calibration graphs using the two types of standards. In other words, standards with or without hydrogen can be used in the same calibration curve without algorithm corrections for the analytical application under investigation.

Regarding the other analytes, different calibration strategies were investigated. Such strategies consisted of evaluating the calibration curves by using five different regions of the afterpeak pulse profile for data treatment: the average of the whole afterpeak region, the average of first peak, the average of second peak, the maximum position of the first peak, and the maximum position of the second peak. As examples, Table 1 and Supplementary Figure S1 collect the different calibration curves obtained for ⁶⁸Zn and ⁵³Cr. Zinc has five natural isotopes but the two most abundant (⁶⁴Zn and ⁶⁶Zn) were found to be not appropriate for rf-PGD-TOFMS measurements since it was observed that the signal intensity saturates easily for samples with high Zn concentration, and calibration curves did not show a linear regression at high concentrations. Thus, ⁶⁸Zn (19.02% isotopic abundance) was selected for measurements. As it is collected in Table 1, the best calibration strategies were found to be the average of the whole afterpeak region and the average of the first peak, showing in both cases good correlation coefficients.

In the case of chromium, ⁵³Cr was selected for measurements. For this isotope, the selection of the calibration strategy turned out to be more critical than for ⁶⁸Zn. Supplementary Figure S1 in the Supporting Information collects the calibration curves and, as can be seen, the calibration graph obtained by selecting the average of the first peak in the afterpeak region showed the best linear correlation coefficient (Supplementary Figure S1b). The comparison between measuring at the maximum of each peak (Supplementary Figure S1d and S1e) and the average of the corresponding peak (Supplementary Figure S1b and S1c, respectively) showed that calibrations using averaged data provided better correlations. This fact can be attributed to the higher number of data points selected, which allow to minimizing the noise. If we compare results for the first peak (Supplementary Figure S1b and S1d) with those for the second peak (Supplementary Figure S1c and S1e), it is evident that the correlation is better using the first peak data, also being better than the correlation shown in Supplementary Figure S1a for the whole afterglow region.

To summarize the work related to this section, the average of the first peak was selected to obtain the calibration curves of Cr, Ni, Mn, and Fe by rf-PGD-TOFMS, whereas the whole afterpeak was selected for Zn and Al. Calibrations for B, Si, O, and P were carried out by measuring the maximum of the afterpeak. Such strategy was also followed for hydrogen calibration (H_3^+ , whose afterglow region only shows one peak).

Quantitative Depth Profiling of TFSCs

The qualitative depth profiles, directly obtained by rf-PGD-TOFMS, were used to calculate the corresponding elemental



Figure 5. Quantitative depth profile (wt% versus depth) obtained by rf-PGD-TOFMS for a-Si:H TFSC deposited on a stainless steel substrate

concentrations, at each position of the depth profile, by making use of the above worked out calibration equations. Measured intensity signals for each analyte (e.g., B) were used to calculate the corresponding element mass content ([B]), at each position of the depth profile, by making use of the corresponding calibration equation (see Figure 2c).

Figure 5 shows the quantitative depth profile obtained by rf-PGD-TOFMS for the TFSC sample under investigation. As can be seen, the thickness for the sum of all the layers is in the order of the expected value (1450 nm) and the identification of the different parts of the photovoltaic device is straightforward. Moreover, dopant elements present in the a-Si:H layer can also be distinguished, even at the low concentration levels existing in these thin films. The values obtained for the depths of the coating layers were similar to the expected nominal depths and Zn, Al, O, H as well as Fe, Cr, Ni, and Mn elemental concentrations (expressed as wt%) agreed well with the nominal composition of the materials employed in the synthesis process.

Conclusions

rf-PGD-TOFMS has been evaluated for the first time here to carry out fast quantitative depth profiling analysis of TFSCs based on a-Si:H. The direct solid analysis of this promising type of samples could present some problems since the amorphous silicon layers contain hydrogen, a light element that could affect the analytical results.

Results showed that rf-PGD-TOFMS is a fast and reliable analytical tool, which allows to determine simultaneously thickness and chemical composition of the investigated solar cells. The success of this research warrants further analytical applications of rf-PGD-TOFMS and underpins this technique as a routine tool for coated samples with thin layers.

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