GD-OES Depth Profiling and Calibration of B Doped Dielectric Layers

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Abstract. Doped Si-based glasses such as boron silicate glass have a variety of applications in photovoltaics. A well suited, fast method for analysing the elemental composition of these layers is glow discharge optical emission spectroscopy. In addition to qualitative depth profiling, quantitative analysis is of special interest. This requires a calibration in the relevant concentration range, which cannot be achieved by certified commercial standards and therefore requires laboratory standards. In context of calibration, the influence of the substrate surface on the depth profile is investigated. It is found that calibration is not unambiguously possible with a rough surface. Optical effects can be identified and a layer system consisting of a SiNx:H interface layer is used, which was optimized by simulating reflection on interfaces using the transfer matrix method so that calibration is possible using such laboratory standards.

INTRODUCTION

Doped Si-based glasses have a variety of applications in photovoltaics, e.g. as dopant sources as well as passivation layer and anti-reflection coating. Nowadays, many solar cell concepts (e.g. passivated emitter, rear totally diffused (PERT) cells) rely on chemical vapor deposited (CVD) layers due to the high parameter variability of the CVD process and the possibility of cost efficient co-diffusion [1].

Using the glow discharge optical emission spectroscopy (GD-OES) measurement technique [2], elemental composition of a sample can be ascertained in form of a depth profile by applying Ar-based reactive ion sputtering. Sputtered atoms from the sample are excited by collisions in the plasma and emit characteristic light during relaxation, which is spectrally analysed. RF pulsing operation mode not only allows non-conductive samples such as glasses to be examined, but also the sputtering rate to be set so low that even layers with a thickness below 20 nm are measurable for depth profiling. In this case, the core equation behind the GD-OES measurement

\[ I_z = \Lambda_z Y_{S,z} Y_{E,z} c_z S_M + I_{b,z}, \]

suggests a linear correlation between detected intensity \( I_z \) and elemental concentration \( c_z \) [3]. Thereby, \( Y_{S,z} \) and \( Y_{E,z} \) denote the sputtering and the emission yield for an element \( z \), respectively, and \( \Lambda_z \) represents the device depending detection efficiency. The weight loss during sputtering time defines the sputtering rate \( S_M = \Delta m/\Delta t \). Dark current and background intensity are expressed by \( I_{b,z} \).

Furthermore, in case of thin layers, the transfer matrix method can be used to calculate the reflection of the incident light from the plasma on the surface and/or interfaces of a layer system with known optical properties [4]. Here, the reflectivity is modelled depending on the sputtering depth utilizing the thicknesses as well as the complex refractive indices of the layers at the corresponding emission lines.

EXPERIMENTAL

During sample preparation, the Float-Zone (FZ) or Czochralski (Cz) crystalline Si substrate is etched and cleaned. Depending on the desired surface topography, the samples are either textured (tex) or polished (KOH) using KOH-based alkaline solutions with or without alcohol-based additives, respectively. An HNO\textsubscript{3}/HF based
solution is used for chemical polishing (cp), in case of Cz-Si. FZ-Si is already polished by the manufacturer, further detailed as ‘pre’-polished (pap).

Boron silicate glass (BSG), silicon nitride (SiNₓ:H) and silicon oxide (SiOₓ) is deposited either using an inductively-coupled-plasma (ICP) plasma-enhanced (PE) CVD tool or an atmospheric pressure (AP) CVD roller system. The grown layers are GD-OES measured with an adapted GDA 750 HR from Spectra Analytik GmbH. To support the GD-OES measurements regarding the calibration, other measurement techniques are applied for obtaining additional properties of the layers, as outlined in Fig. 1. Scanning electron microscopy pictures are taken in order to understand the sputtering process on rough surfaces. Layer thickness and optical properties are measured by ellipsometry. Applying contact-profiliometry measurements of GD-OES craters combined with ellipsometry measurements and weighing on a micro scale, the layer thickness, the density of the layer and the substrate as well as the sputtering rate $S_M$ can be determined.

![FIGURE 1. Schematic process flow of samples shown in the results section. Dashed arrows indicate alternative process sequences regarding the general process flow due to distinct substrate investigations.](image)

RESULTS

Sputtering Process

The SEM image in Fig. 2 shows a textured Si substrate surface before (Fig. 2(a)) and after (Fig. 2(b)) the sputtering process during the GD-OES measurement. As can be seen by comparing the pictures, the sputtering front does not move into the substrate over the entire surface in the same way, as might initially be expected. Instead, the pyramids seem to be smoothed over time. The sputtering process takes place due to Ar ions which are ionized and accelerated due to the applied electric field in the sheath potential of the plasma. Due to the rough surface of the textured substrate, non-homogeneously spaced field lines are formed. As the field lines accumulate at the pyramid peaks, these are preferentially sputtered while the crater front is moving into the substrate.

![FIGURE 2. SEM pictures taken before (a) and after (b) a $t = 200$ s GD-OES sputtering process step on KOH-textured Cz-Si.](image)

However, the difference in height between the surfaces highest and lowest point after sputtering step is still in the micrometre range so that the surface is still considered to be “rough”.

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Figure 3 shows the dependency of relative sputtering rate \( q = \frac{S_{\text{M}}}{S_{\text{Fe}}} \), whereby \( S_{\text{Fe}} \) describes the sputtering rate of a certified Fe standard, on the base doping and the surface of the Si substrate. For industrially pre-chemically polished (pre-cp) FZ-Si n-type as well as p-type samples, one can observe a higher relative sputtering rate with increasing base doping concentration. This can be explained by the higher conductivity of the substrate doped with more dopants. The higher the conductivity of the sample, the stronger is the influence of the applied bias voltage on the kinetic energy of the Ar ions leading to a higher current of the ions towards the sample in the plasma sheath potential. Thus, more Ar ions can hit the sample during a certain time period but there is also the possibility that more target atoms can be sputtered by one Ar ion.

Furthermore, for Cz-Si samples different substrate surfaces show a variation in relative sputtering rate. For n-type as well as for p-type, the textured samples (tex) have the highest relative sputtering rate followed by the samples with saw damage (sd), HNO\textsubscript{3}/HF based chemical polishing (cp) and KOH etching (KOH). As the surface factor decreases in the same order, this behaviour can be attributed to it. A larger surface within the sputtering area provides more possible Ar ion collisions with the sample. This also confirms the early finding concerning the equally strong sputtering process on all sides.

Regarding the substrate doping, qualitative depth profiling of deposited layers is of special interest because of the clearly visible influence of the dopant concentration on the intensity curves \( I_z \). Figure 4 shows the GD-OES measured depth profile of an APCV-deposited BSG layer on two chemically polished n-type FZ-Si substrates with different base doping. Considering the optical properties determined by spectral ellipsometry, it can be observed that
the sputtering time of the same layer takes longer on the less doped substrate and that the intensity decreases with longer sputtering time. This means that the sputtering rate of the same matrix is changing with base doping.

In conclusion, for qualitative depth profiling, samples are only allowed to be compared physically with the same matrix as well as the same substrate. This effect does not influence quantitative depth profiling. Therefore, it can be used that the concentrations (in at\%) of the single matrix elements always sum up to one.

**Surface Influence on Depth Profiling**

Figure 5 shows GD-OES depth profiles of a multilayer system consisting of an APCVD-grown BSG and silicon oxide (SiO\textsubscript{x}) layer on both FZ-Si (Fig. 5(a)) and Cz-Si (Fig. 5(b)) substrates.

Compared to the B intensity curve of the reference sample in Fig. 5(a), the profile of the KOH-etched Cz sample in Fig. 5(b) shows a broader left flank (dashed box) starting at $t = 0.5$ s, which is a newly discovered effect.

![Figure 5](image)

**FIGURE 5.** GD-OES measured depth profiles of BSG/SiO\textsubscript{x} stacks on chemically polished (pre-cp, see above) FZ-Si (a) and on (standard concentrations for photovoltaics) KOH-etched planar Cz substrate (b). The SiO\textsubscript{x} and BSG layer are marked by arrows labelled with $t_{1,3}$ and $t_{2,4}$, respectively, and the substrate region is illustrated with a streaked background. In this figures, signal intensities of O and H are shown for better identification of layer interfaces.

This can be explained with the surface topography of the Cz-Si sample. Similar to an alkaline texture solution, the KOH solution etches strongly anisotropically. Despite possible subsequent short chemical polishing, the sample has a topography of facetted terraces with (111)-oriented side surfaces on the total surface. On (111)-oriented surfaces, the doped layers are thinner possibly due to the angle relative to the deposition and the growth rate of the layer on the crystal orientation.

This is also shown by the approximately $t_{1} - t_{3} = 0.9$ s shorter sputtering time of the silicon dioxide layer and $t_{2} - t_{4} = 0.7$ s shorter sputtering time of the BSG layer on the (111)-oriented areas of the sample. As shown before, the layers in the glow discharge source are equally sputtered on all sides. Before the SiO\textsubscript{x} layer on the (100)-oriented surface is detached, the sputtering front already moves into the BSG grown on the (111)-oriented surface. The result is the increase of the B signal in Fig. 5(b) (dashed box).

The broadened right flank (dotted box) at $t = 6.0$ s in the B intensity curve of the reference sample (Fig. 5(a)) must not be confused with the effect described in this section. The decreasing of the Si and B signal curve at the same time indicates a change in the sputtering rate. This is due to the base doping, mentioned in the section above.

In conclusion, this means that calibration can only be performed on a flat substrate surface as not to have a temporal distortion of signals. Furthermore, the way in which sputtering occurs is the reason why it is detrimental for reliably measure on rough surfaces (e.g., textured) or to derive a quantitative depth profile from such topography.

**Influence of Optical Effects on Depth Profiling**

For calibration purposes, an interface layer (optimized SiN\textsubscript{x}:H) was deposited in between the layer to be measured (BSG) and the Si substrate to clarify if it might alleviate certain signal artefacts. Figure 6(a) shows the GD-OES measured depth profiles of a reference sample without the interface layer and a layer stack with the interface layer. For the reference sample (dashed line), oscillations in the B signal can be seen that cannot be
attributed to the layer of known constant B concentration. It suggests a change in doping that in reality does not exist.

From the modelled reflectivity for the relevant emission wavelengths in Fig. 6(b), it can be stated that the oscillations which are inconsistent with the physics of the sample are related to the optical effects described below. It is clearly visible that the Si signal as well as the B signal curves are similar to the reflectivity curve.

Reflection at interfaces of layers arises due to different refractive indices. The thin layer acts as interference layer. Due to the sputtering process, the layer thickness is reduced over time. This leads to a periodic reflectivity which influences the measured signal. However, in the intensity curve for B, it can be shown that a higher reflectance does not necessarily result in a higher measured intensity, but that the oscillation described above is more pronounced.

![Graphs](image)

**FIGURE 6.** Comparison between (top) the GD-OES measured depth profiles of a sample with SiNₓ:H interface layer (b, solid line) and without interface layer (a, dashed line) and (bottom) the simulation of the reflection by the transfer matrix method, respectively with and without the interface layer. The substrate and interface layer region is marked by streaked lines.

Considering the refractive indices of doped silicate glass (e.g. BSG) and Si, SiNₓ:H is a good choice for reducing the reflectance due to its intermediate refractive index as well as its light absorbing properties in the UV region in which most of the emission lines are located. In Fig. 6(a) it can be observed, that no oscillations in the B signal (orange curves) for the layer stack with a SiNₓ:H intermediate layer are detectable. This is also confirmed by the much smaller reflectance simulated as shown in Fig. 6(b) (orange curves; observe scaling).

**Laboratory Standards**

Applying such an interface layer, it is possible to produce laboratory standards with different B contents by varying the diborane flow during PECV-deposition. Using ICP-OES, the aerosol in plasma phase from in HF dissolved BSG layers was analysed. In Fig. 7(a) the so measured B concentration is plotted depending on the diborane flow $Q_{B_2H_6:H_2}$ normalized on the total gas flow $Q_{total}$. The increase of concentration $c_0$ with higher dopant
gas flow confirms the suitability of the laboratory standards. The greatest advantage of the laboratory standards is the coverage of the relevant concentration ranges. As shown in Fig. 7(a), the boron concentration can be adjusted linearly with the diborane gas flow in this range. In addition, the standards are easily reproducible and can also be used as re-calibration standards.

Figure 7(b) shows the GD-OES measured depth profiles of the laboratory standards. The average of the flat region of the relative B intensity $I_B$ is determined for the correlation to the ICP-OES measured concentration $c_B$.

**Calibration**

Calibration is carried out using the product of relative sputtering rate $q$ and the measured concentration $c_B$. The so calculated virtual concentration $q \cdot c_B$ is shown in Fig. 8 depending on the relative B intensity $I_B$ for the laboratory standards.

Using a weighted polynomial approach it can be found that literature’s first suggestion of a linear correlation is imprecise. By calculating the coefficient of determination a parabolic correlation can be found. The calibration curve shown in Fig. 8 is fitted with a fixed zero concentration point marking the background intensity.

The derived parabolic behaviour can be explained by the phenomena of self-absorption [5]. Self-absorption can occur for some emission lines (e.g. resonance lines) and leads to non-linear behaviour - especially for high B doping concentrations typical for BSG films - due to fluctuation of the plasma density.

**CONCLUSION**

In conclusion, GD-OES is a measurement technique for determining elemental concentration and composition in thin dielectric layers. For qualitative and especially for quantitative analysis, planar surfaces are advantageous for clearly identifiable signals. Thereby, the influence of the substrate has to be considered. On planar surfaces, optical
effects occur due to interference and reflection on interfaces which can be confirmed by simulation. A SiN$_x$:H interface layer allows signal measurement with less reflection and thus the development of laboratory standards for calibration. Using relative sputtering rates and virtual concentrations, a matrix independent calibration is possible taking the phenomena of self-absorption into account which is expressed in non-linearity for high B concentration.

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