In-line plasma-chemical etching of crystalline silicon wafers at atmospheric pressure using FT-IR spectroscopic process control

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ABSTRACT

The etching technology currently used in the solar industry is mostly based on wet chemical processing. Plasma-enhanced dry chemical etching at atmospheric pressure is an alternative to the existing technology, especially when combined with similar process technologies, for example plasma-enhanced deposition techniques at atmospheric pressure, to provide a continuous in-line processing of crystalline silicon solar cells. This paper presents the use of plasma chemical etching using Fourier Transform infrared (FT-IR) spectroscopy to monitor different silicon wafer processing steps as an alternative to the widely used wet chemical processing approach.

Introduction

Silicon etching processes are essential steps in crystalline silicon solar cell manufacturing. Currently, industrial production of silicon solar wafers is mostly based on wet chemical processing. Etching steps like saw damage removal, surface texturing, edge isolation, and phosphorous silicate-glass removal are often done in acidic or alkaline solutions at elevated temperatures. The drawbacks of this process are the needs for large volumes of distilled water, the chemical waste disposal requirements, as well as the high mechanical impact on the wafer [1].

Etching of crystalline silicon can also be carried out by plasma technology. Plasma-chemical etching has attracted recent interest for economic and technological reasons [2], especially when realised at atmospheric pressure. Advantages can be seen in:

- High throughput for in-line solar wafer processing
- Cost efficiency due to decreased breakage rate of thin solar wafers by soft processing and reduced handling due to in-line processing
- One side treatment for texturing
- Adaptive for different etching steps
- Reduced chemical waste.

Based on a linearly extended DC arc with a working width of 150mm for plasma activation, an innovative atmospheric pressure plasma etching technology has been developed. The remote injection of the etching gas prevents plasma source damage due to chemical attack of etching radicals. Fluorine radicals generated from NF_3 and SF_6 by an argon-nitrogen remote

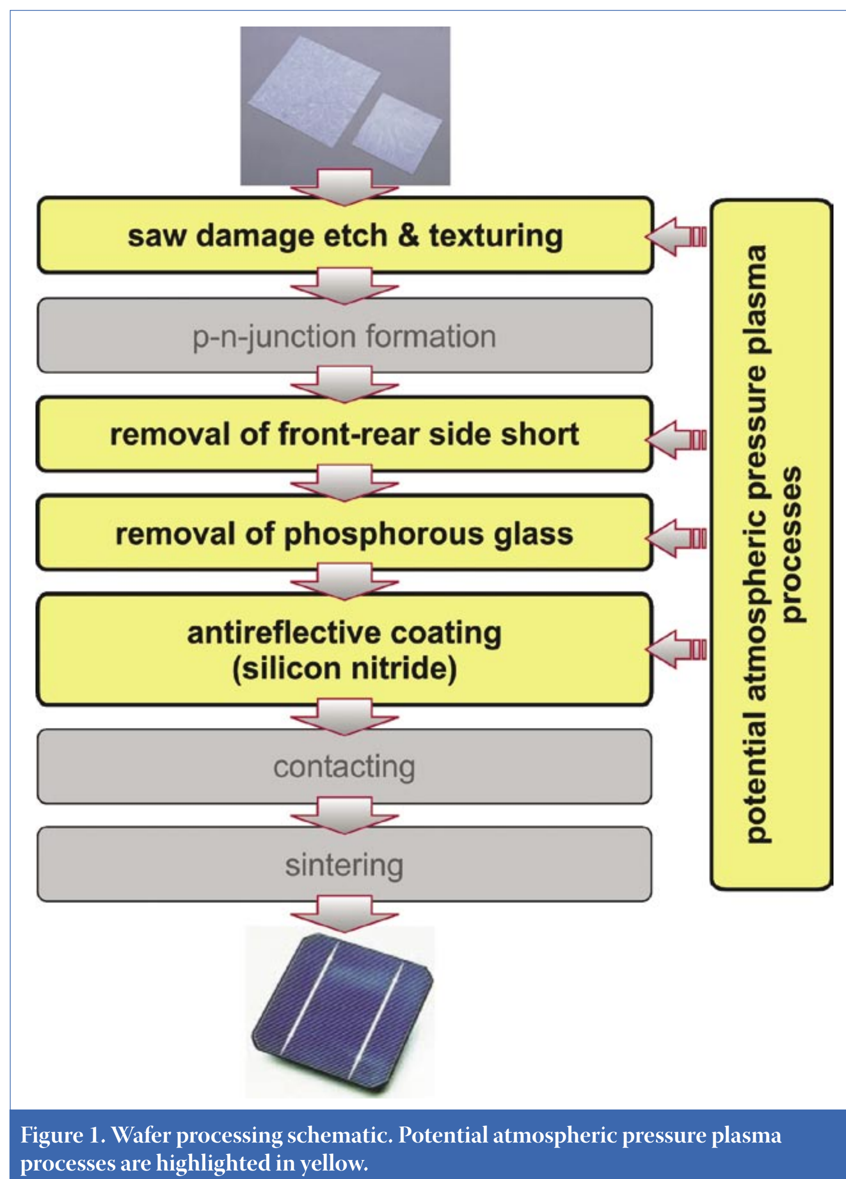

Figure 1. Wafer processing schematic. Potential atmospheric pressure plasma processes are highlighted in yellow.

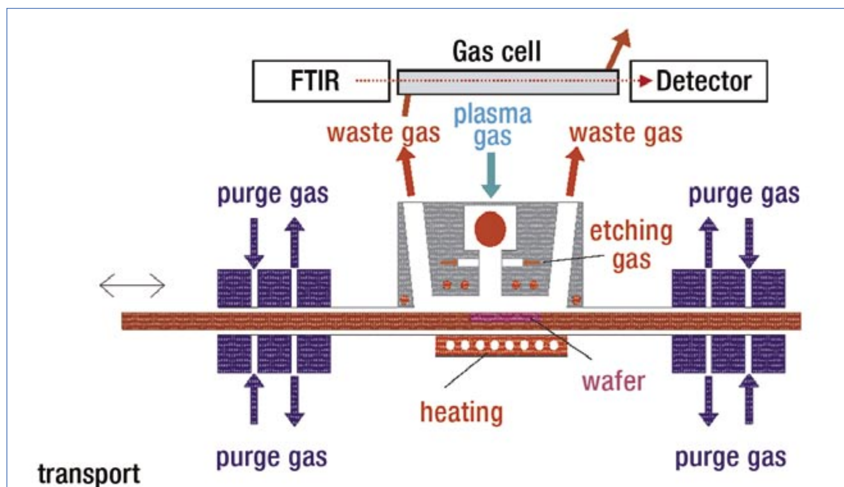

Figure 2. Principle of atmospheric pressure plasma etching equipment and FT-IR measurement device.

plasma have been successfully utilized to etch (100) monocrystalline-Si wafers.

Fourier Transform infrared (FT-IR) spectroscopy was applied to monitor different silicon wafer processing steps. Instantaneous determination of the current etching rates is achieved by the analysis of the waste gas during wafer treatment. This non-destructive measurement device has the potential to be inserted into a plasma-chemical silicon wafer processing line to monitor processes such as saw damage etching, edge isolation and phosphorous silicate-glass removal.

Plasma technology developed at Fraunhofer IWS works at atmospheric pressure and is able to cover not only plasma etching but also plasma-enhanced chemical vapour deposition (AP-PECVD). The deposition technique was successfully applied to coat crystalline silicon solar wafers with SiN_x as the antireflective and passivation layer [3]. Figure 1 shows the processing sequence of crystalline silicon wafers. Saw damage etching, surface structuring, front-rear side short removal and etching of the phosphorous silicate-glass are demonstrated with atmospheric pressure arc plasma technology. The feasibility of edge isolation was proved several times by industrial tests [4].

Launching a new technology based on atmospheric pressure plasma etching processes leads to the important question of process control during wafer processing, especially when aimed at industrialisation. The method of choice should be non-destructive, fast, and easy to handle, so that the wafers do not have to undergo an extra handling step. Time-resolved FT-IR spectroscopy is able to detect volatile silicon species occurring during plasma-chemical etching of silicon wafers, which provide instantaneous information about the current etching rate and the etched depth of the wafer; this data in turn plays an important role when a certain thickness of the saw damaged layer has to be removed at the beginning of the processing chain. Monitoring of phosphorous gas species can be used for controlling the process of phosphorous silicate-glass etching in terms of front-side or back surface etching after p-n junction formation. In-line FT-IR spectroscopy analyses the exhaust gas to obtain relevant information about the etching progress and thus is a promising non-destructive measurement method.

Etching and monitoring equipment

Etching of crystalline silicon solar wafers is carried out by an innovative atmospheric pressure plasma process. This technology is based on a linearly extended arc discharge with a working width of 150mm; as well as the 150mm DC arc, a plasma source with an arc length of 250mm has been established at Fraunhofer IWS, rendering the processing of 6-inch wafers possible. The plasma is generated in the DC arc while argon and nitrogen, which act as plasma gases, flow in a perpendicular direction through the arc axis (see Figure 2), resulting in a remote plasma. Detailed information about the plasma source assembly can be found elsewhere [5, 6, 7].

The etching reactor design and the FT-IR measurement device are also depicted in Figure 2. Since the technology works at atmospheric pressure, simple purge gas curtains on the entrance and on the end of the reactor prevent the leakage of the etching gases, also providing a controlled atmosphere inside the reactor. A careful design of the reactor based on fluid dynamic modelling is necessary to this process.

The core piece of the reactor is the plasma source with a specially designed plasma gas distributor, a remote precursor injection system and double-sided waste gas extraction channels, which direct the waste gas to an abatement system for treatment. Leaving a small distance between the plasma source and the etch gas injection system leads to better utilization of the etching gas. Since the ions in the plasma recombine early, no ion bombardment of the wafer takes place and hence no wafer damage occurs. Etching gases are not supplied directly through the plasma source to prevent the possibility of damage due to chemical attack.

During etching, the silicon wafers are placed on a carbon substrate holder, allowing the wafers to be heated up to 400°C. The wafer itself is fixed on the substrate holder by a suction system and passes dynamically under the plasma source with velocities up to 100mm/s.

Typical experimental parameters for plasma enhanced chemical etching are summarized in Table 1. In this case, the etching gases used were SF_6 and NF_3.

Plasma etching processes carried out in the described atmospheric pressure plasma etching equipment were monitored by Fourier Transform Infrared absorption spectroscopy using a Bruker Matrix FT-IR spectrometer. Table 2 summarizes the acquisition parameters utilized for this example.

Parameter	Parameter range
Plasma/Carrier gas	Ar / N_2
Voltage (V)	190 – 240
Current (A)	80 – 100
Power input (kW)	15 – 24
Plasma gas flow (slm)	45 – 65
Etching gases	NF_3, SF_6
Amount of etch gases (slm)	0.3 – 2
Temperature of wafer (°C)	300 – 400

Table 1. Typical parameter range for the 150mm DC arc plasma source and for the plasma etching process.

Parameter	Range
Detector	N_2-MCT (mercury-cadmium-telluride)
Measurement range (cm^{-1})	500 - 4500
Spectral resolution (cm^{-1})	4
Time resolution (s)	1
Optical path length (m)	0,2

Table 2. Acquisition parameters of waste gas measurement.

The measurement was performed in the waste gas line (see Figure 2) to determine the chemical composition of the waste gas. Initially, measurements of pure etching gases without plasma were performed and compared to the spectra of the etching gases with plasma impact to estimate their decomposition rates. Measurements during the plasma etching of 5-inch (125 × 125mm^2) alkaline (KOH) textured monocrystalline silicon wafers and 5-inch alkaline textured monocrystalline silicon wafers after $POCl_3$ diffusion (P-doped) were carried out.

Results of in-line FT-IR spectroscopy

Figures 3 and 4 show the spectra of the precursors SF_6 and NF_3 as well as their decomposition in the plasma. The comparison of the spectra in Figure 3

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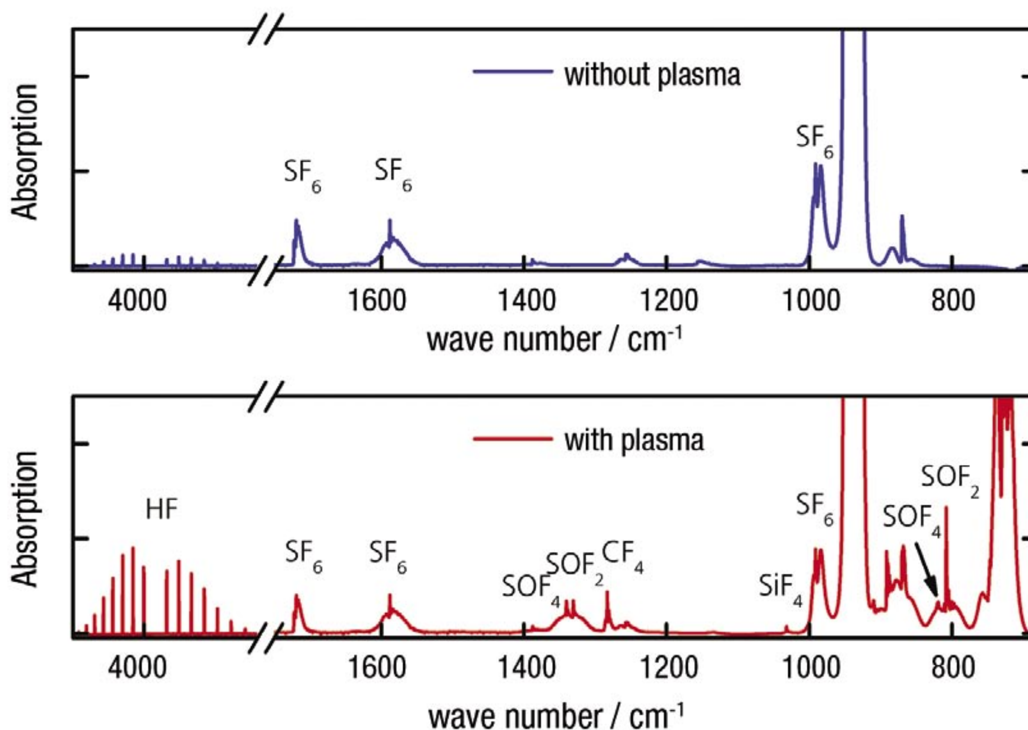

Figure 3. IR spectra of pure SF_6 (top) and during SF_6 plasma decomposition (bottom).

(SF_6) and Figure 4 (NF_3) indicates that the plasma plays a crucial role for an effective etching gas decomposition. According to the spectra, a decomposition rate of 15% for SF_6 and 90% for NF_3 can be calculated; the reason for this difference can be found in the different average energies for S-F (368 kJ/mol, 298 K) and N-F (278 kJ/mol, 298 K) bonds. In both cases the formation of active fluorine species due to the plasma impact can be assumed, leading to the components HF ($3960cm^{-1}$), SOF_2 ($810cm^{-1}$, $1335cm^{-1}$) and SOF_4 ($820cm^{-1}$, $1890cm^{-1}$) when a low concentration of water vapour is present in the reaction chamber and CF_4 ($1280cm^{-1}$) due to a slight etching of the graphite substrate holder.

Probably, silicon deposits of preceding etching cycles at the reactor walls and in the waste gas line lead to the appearance of SiF_4 traces at $1030 cm^{-1}$.

During the plasma etching of the silicon wafer, SiF_4 was identified as the volatile key species. Figure 5 shows the SiF_4 IR-absorption band at $1030cm^{-1}$ during SF_6 and NF_3 etching.

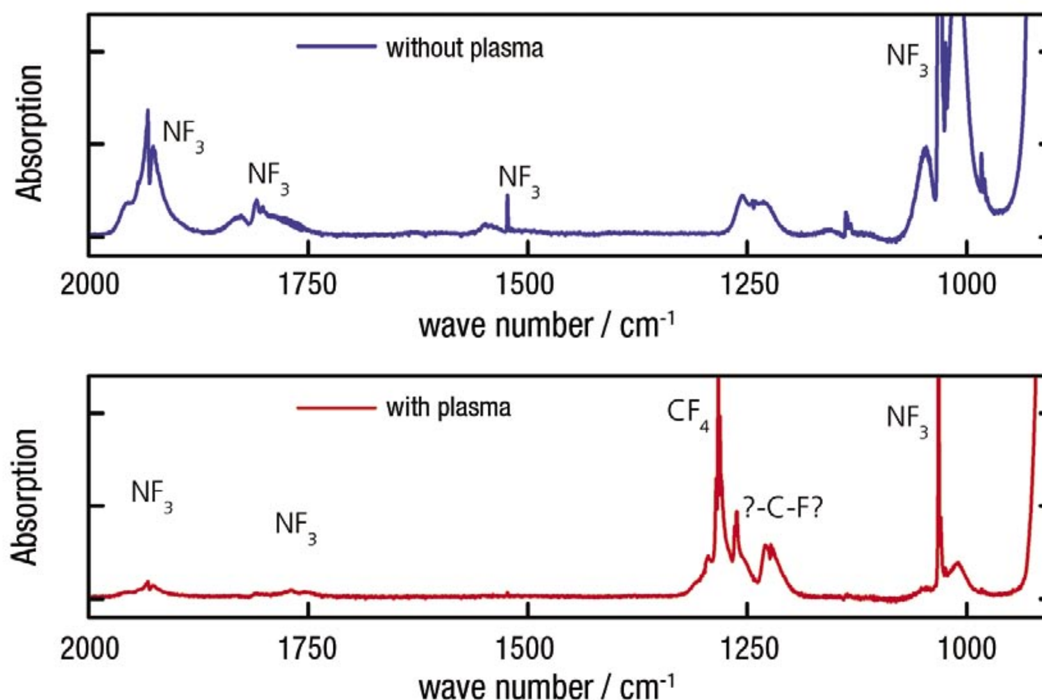

Figure 4. IR spectra of pure NF_3 (top) and during NF_3 decomposition in plasma (bottom).

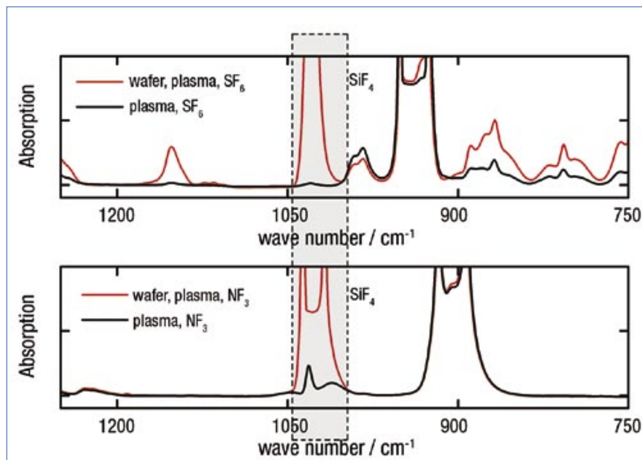

Figure 5. IR spectra during plasma-enhanced chemical etching of silicon wafers with SF_6 (top) and NF_3 (bottom) (reference measurement without wafer depicted in black).

As the high concentration of SiF_4 leads to too high absorbance values at 1030cm^{-1} and also completely overlaps with the NF_3 absorption (Figure 5, bottom image), the quantitative evaluation of SiF_4 concentration was carried out at 1191cm^{-1} (not shown in Figure 5 due to the y-axis scale). It was found that the measured SiF_4 IR-absorption could be directly related to the weight loss of the wafer, which was determined by gravimetric measurements.

Based on the calculated weight loss from SiF_4 IR-absorption or gravimetry after etching, the dynamic etching rate in [µm · m/min] can be determined by the following equation:

- dynamic etching rate = Δm / wafer factor (f(A, ρ)) * R,

while the etched thickness in [µm] can be determined by:

- etched thickness = Δm / wafer factor (f(A, ρ)

where Δm is the weight loss of the wafer, A the wafer area, ρ the density of the silicon wafer, and R the reactor residence time of the wafer.

Both the etched thickness (Figure 6) and the etching rate can therefore be calculated in real-time using in-line FT-IR spectroscopy.

In-line FT-IR measurements can be applied to determine the weight loss of the wafer, but can also monitor the edge isolation process step on the rear side or the phosphorous silicate glass (PSG) etching step on the front side after $POCl_3$ diffusion. In this case the key species is POF_3, which can be found at 1416cm^{-1}. Figure 7 points out the time-dependent concentration of SiF_4 and POF_3 during dynamic PSG removal (the wafer passed through the reactor several times). POF_3 is present only during the first wafer run due to the thin PSG layer on the front side of the wafer, whereas SiF_4 is detectable during the whole six runs. Furthermore, the progress of the process can be monitored. The course of SiF_4 concentration shows the movement of the wafer into and out of the etching zone.

Given that all measurements are carried out at the waste gas line, the infrared spectroscopy provides an efficient and non-destructive tool for direct in-line process monitoring and process control. It allows precise control of the removal of silicon and PSG layers from the wafer.

Conclusion

In-line plasma-chemical etching of crystalline silicon solar wafers at atmospheric pressure and FT-IR spectroscopic measurements for quantitative analysis of the decomposition products of the etching gas NF_3 and SF_6 in the plasma were demonstrated as alternatives to the wet chemical processing method. NF_3 shows the highest decomposition rate in the plasma due to its lower binding energy compared to SF_6, while the same method was used to monitor the waste gas during plasma chemical etching of crystalline silicon wafers.

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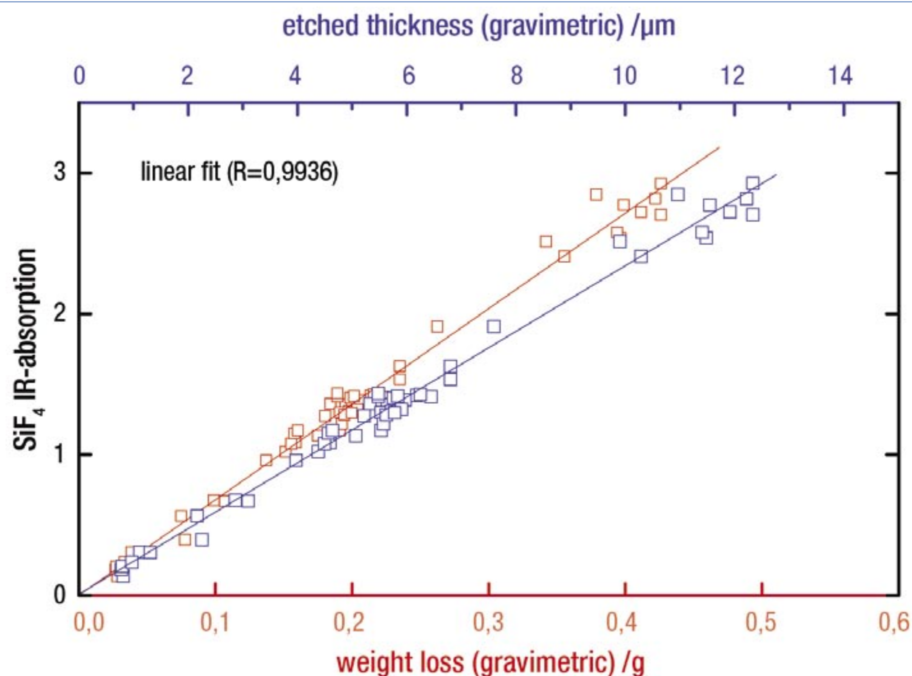

Figure 6. Relationship of SiF_4 IR absorption during wafer etching showing weight loss (x-axis 1) and etched thickness (x-axis 2). Etched thickness is determined by gravimetric measurements after wafer etching with SF_6 and NF_3.

The study identified SiF_4 as the main reaction product during etching, the IR-absorption of which is linearly related to the weight loss of the etched wafer. Thus, SiF_4 monitoring by FT-IR spectroscopy allows the determination of the etched thickness and the dynamic etching rates of the wafers. A FT-IR spectroscopic process analysis for phosphorous silicate glass (PSG) etching was demonstrated by monitoring POF_3. Since the concentrations of the etching products can be mapped, the progress of the etching process can be recorded precisely.

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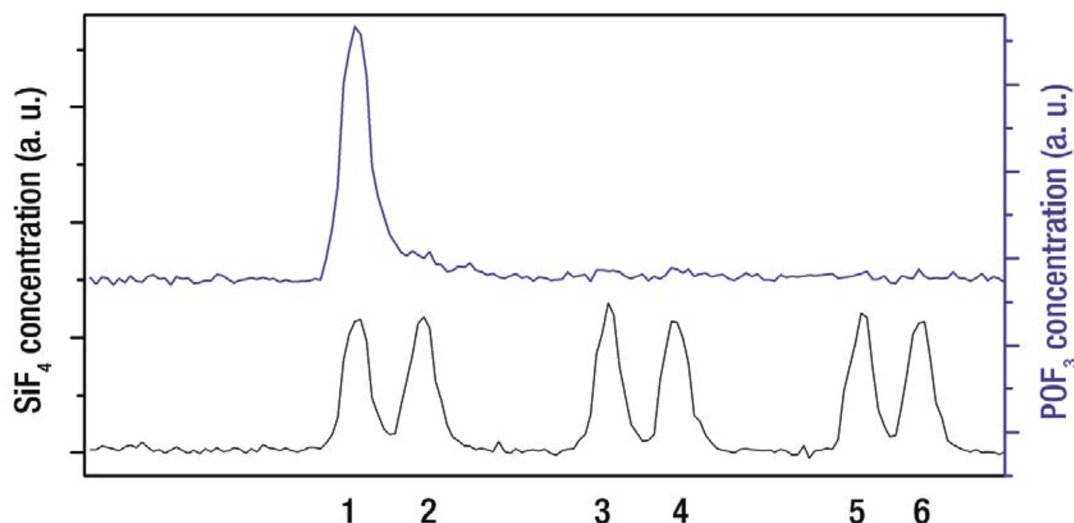

Figure 7. Time-dependent concentration of SiF_4 and POF_3 during phosphorous silicate glass etching (etching gas NF_3).

About the Authors

Dorit Linaschke has held the role of researcher and project manager in the CVD thin-film technology group at Fraunhofer Institute for Material and Beam Technology since 2005. She graduated with a Dipl.-Ing. in material science in 2002 from the Technical University Bergakademie in Freiberg and in 2004 she received an M.Sc. degree in molecular bioengineering from the Technical University, Dresden.

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