SiO_2 Dry Etching with the Expanding Thermal Plasma Technique

The possibility for Phosphorus Silicate Glass (PSG) etching for Solar Cell Applications

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Outline

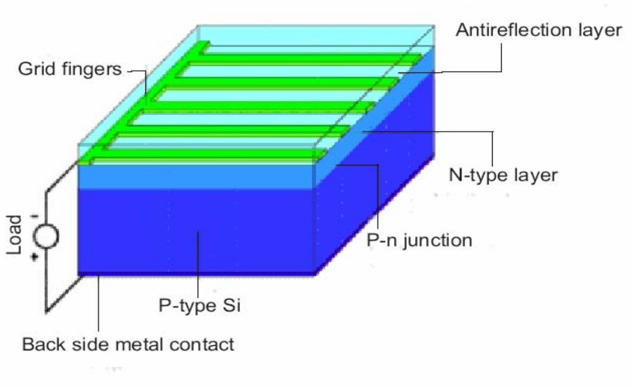
- **Motivation**
  - plasma processing for solar cells:
    - To lower the cost of PV industry
  - Expanding Thermal Plasma:
    - Solar cells processing

- **Experimental setup**
  - Expanding Thermal Plasma Technique

- **Experimental results**
  - *In situ* and *ex situ* spectroscopic ellipsometry measurements
  - photoconductance decay measurements
- **Conclusions/Outlook**

Solar cells - status and perspective

- ❑ Recently, solar cells are wafer-based crystalline silicon technology.
  - ~ 90 % of current production solar cells
  - High efficiency
    - Lab: 24.7 %, module: 22.7 %
- ❑ Various thin film technologies are developed (second generation)
  - Relatively cheap, moderate efficiency
    - Lab: 18.4 %, module: 13.4 %
- ❑ New technologies (third generation)
  - Very cheap, moderate efficiency (~10-15 %)
  - Relatively expensive, very high efficiency (> 30 %)



Schematic illustration of the solar cell structure

Solar cell processing sequence

Standard industrial solar cell

Process	Conventional wet process (reference)	
Saw damage removal	NaOH	
Pre-diffusion cleaning	HNO_3 etch	
Emitter diffusion	$POCl_3$ diffusion	
PSG removal	HF-Dip	
Anti-reflection coating	SiN_x deposition	
Metallization	Front and back contact screen printing	
	Co-firing	

Solar cell processing sequence

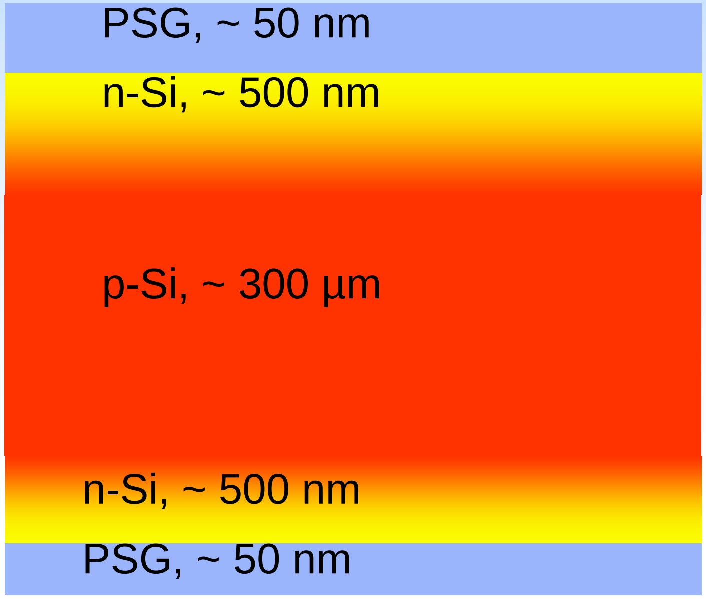
Replacing wet processing by dry one

Process	Conventional wet process (reference)	Dry plasma process
Saw damage removal Pre-diffusion cleaning	NaOH HNO_3 etch	SF_6 plasma
Emitter diffusion	$POCl_3$ diffusion*	
PSG removal	HF-Dip	CHF_3/SF_6 plasma Surface conditioning and cleaning
Anti-reflection coating	SiN_x deposition	
metallization	Front and back contact screen printing Co-firing	

*Also $POCl_3$ diffusion can be replaced by dry deposition of phosphorous containing glass

Phosphorous Silicate Glass (PSG) etching
SiO_2 etching

- Emitter diffusion:
  - Emitter diffusion is carried out by using $POCl_3$ as dopant source in O_2 atmosphere at 800°-900°C.



- PSG layer normally is removed by HF dip (wet chemically etching).
- PSG has very similar properties of SiO_2

SiO_2/PSG etching typical results

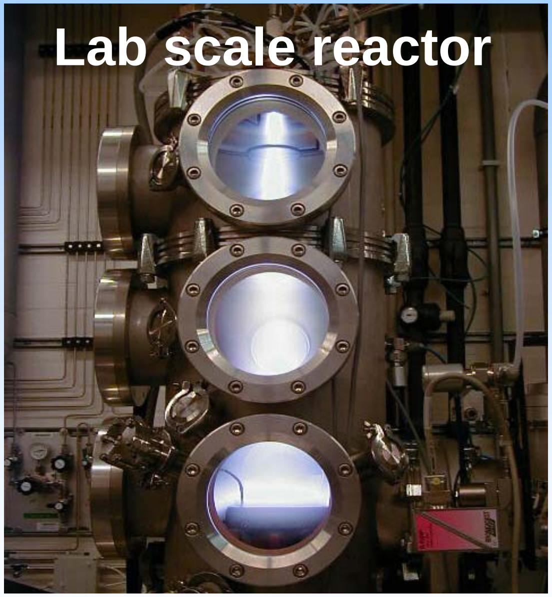
Plasma etching system	Etching gases used	Etch rate		Reference
RIE system	CHF_3/O_2	17 nm/min (PSG)		S. Schaefer et al., 1999
MWRIE	CF_4/C_2H_4	~ 30 nm/min (SiO_2) optimum selectivity		J. Rentsch et al., 2003
ECR-RIE	$CF_4/C_2H_4/Ar$	37 nm/min (SiO_2)		K. Roth et al., 2004
PECVD batch reactor	CHF_3/SF_6	~ 3 nm/min (PSG)		A. Nositschka et al., 2003

Expanding Thermal Plasma Technique (ETP)

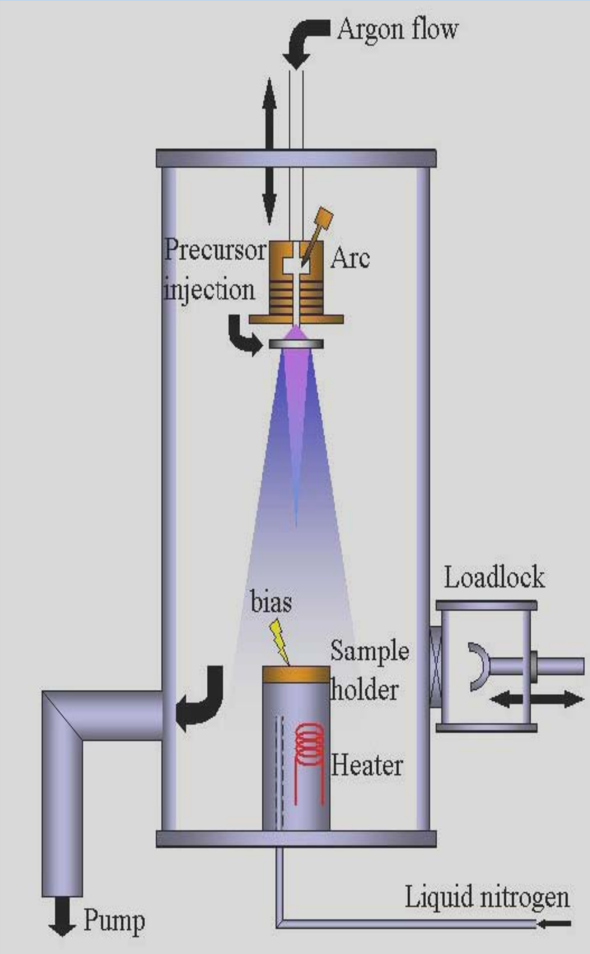
- First patent 1989 from Eindhoven Univ.
- Many materials by choice of precursor
  - a-Si:H
  - μc-Si:H
  - a-SiN$_x$:H
  - a-C:H
  - SiO$_2$
- High rate process (4 – 20 nm/s)
- Remote operation

- Industrialized by OTB Solar for a-SiN$_x$:H deposition (DEPx)
  - Big industrial solar cell manufacturers

W. M. M. Kessels et al., Journal of Vacuum Science & Technology A, 20(5), 2002
B. Hoex et al., Prog. Photovolt: Res. Appl. 2005; 13:705



Expanding Thermal Plasma Setup



Cascaded arc plasma source

high pressure (~ 600 mbar)

$n_e \sim 10^{22}\ m^{-3}$; $T_e \sim 1$ eV

ϕ_{Ar}: 25 – 100 sccs

Expanding plasma

low pressure (~ 0.35 mbar)

$n_e \sim 10^{17}$-$10^{19}\ m^{-3}$, $T_e \sim 0.3$ eV

Precursor injection

Trifluormethane (CHF_3)

Sulfur Hexafluoride (SF_6)

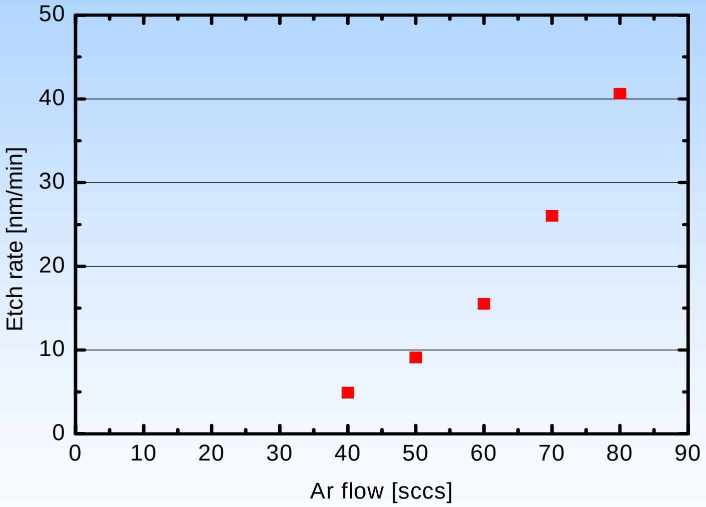
Sinusoidal 13.56 MHz RF substrate bias technique (ion bombardment)

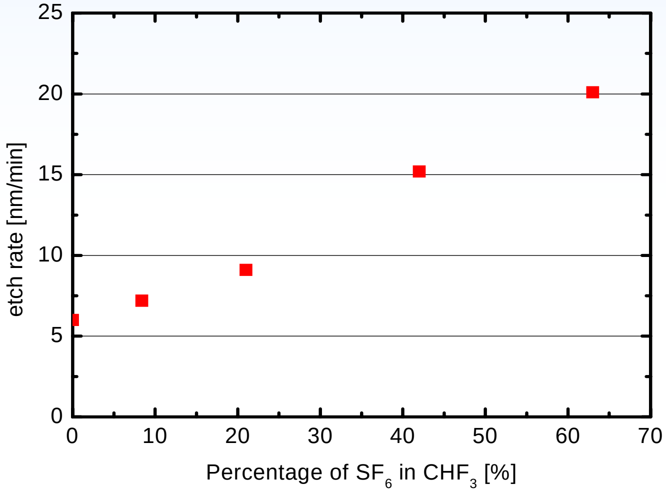
☐ Basic principle:

- Efficient argon plasma generation at high pressure
- Supersonic expansion from high to low pressure
- Plasma chemistry separated from plasma generation
- Low electron temperature: ion-induced reactions
- Controlled substrate conditions (Temperature and external RF-bias)

Experimental results

- Effect of gas flow rates on the oxide etching:
  - Etch rate increases by increasing of the Ar flow. This is due to the increasing of the plasma source efficiency.





- High SF_6 flow gives higher SiO_2 etch rate due to the increase of the active F containing species.

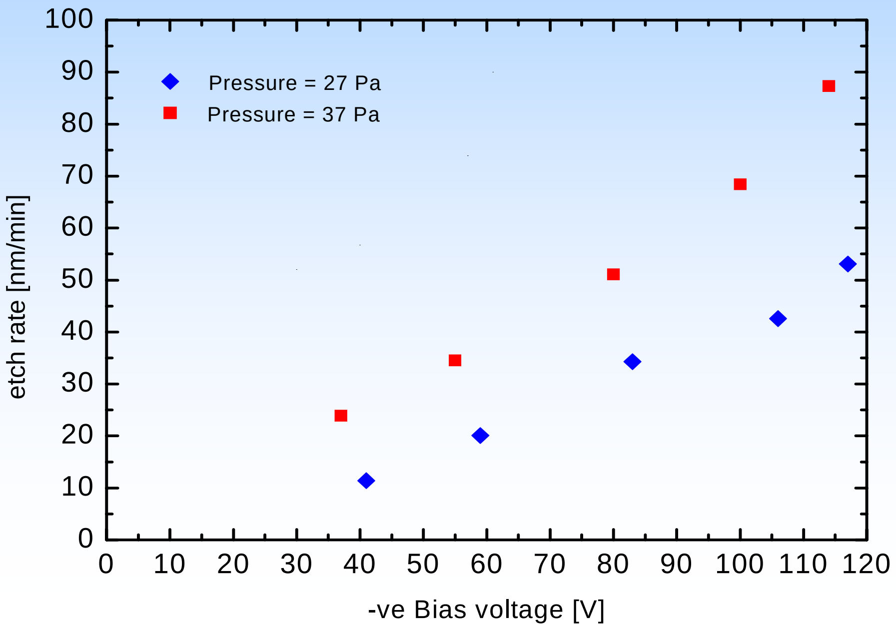
Transfer from Ar^+ to molecular ions

$Ar^+ + SF_6 \rightarrow Ar + SF_5^+ + F$ (Charge transfer)

$SF_5^+ + e^- \rightarrow SF_4 + F$ (Dissociative recombination reactions)

Substrate bias voltage dependence

- Etch rate is controlled by ion flux and ion energy.
- Ions for bombarding the wafer surface arise from RF biasing

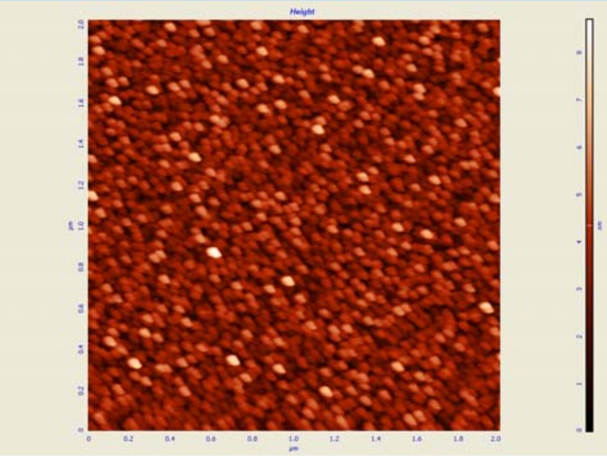


rf power range (5 - 40 watt)

- At higher pressure:
  - smaller beam diameter
  - larger etching radical flux flowing to the substrate.

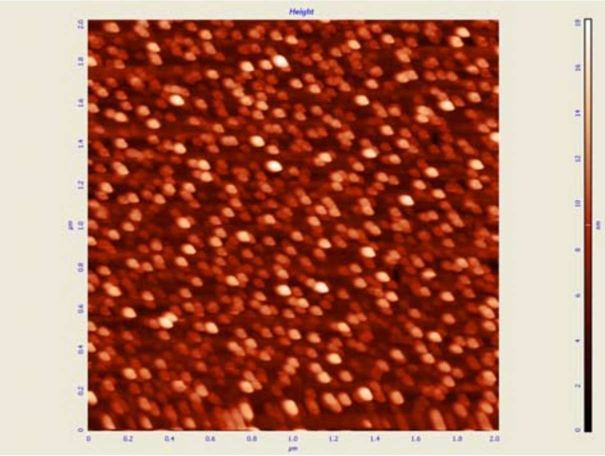
Impact of substrate biasing on surface roughness

AFM images of SiO_2 film surface



0 V substrate bias

- etch rate = 9.1 nm/min
- RMS roughness = 1.05 nm



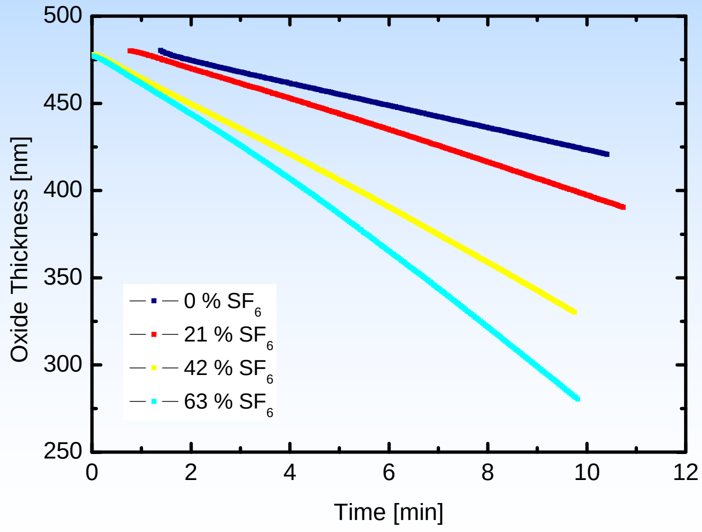
- 130 V substrate bias

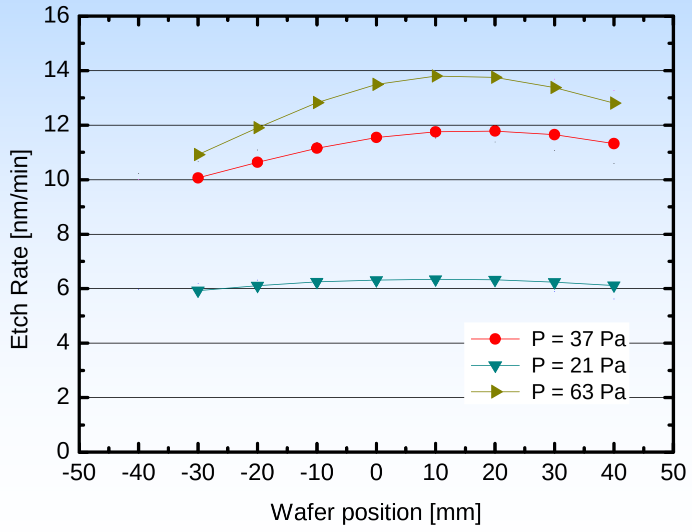
- etch rate = 40.7 nm/min
- RMS roughness = 2.44 nm

High bias gives rougher SiO_2 film surface.

Spectroscopic ellipsometry

SiO_2 etch uniformity characteristics



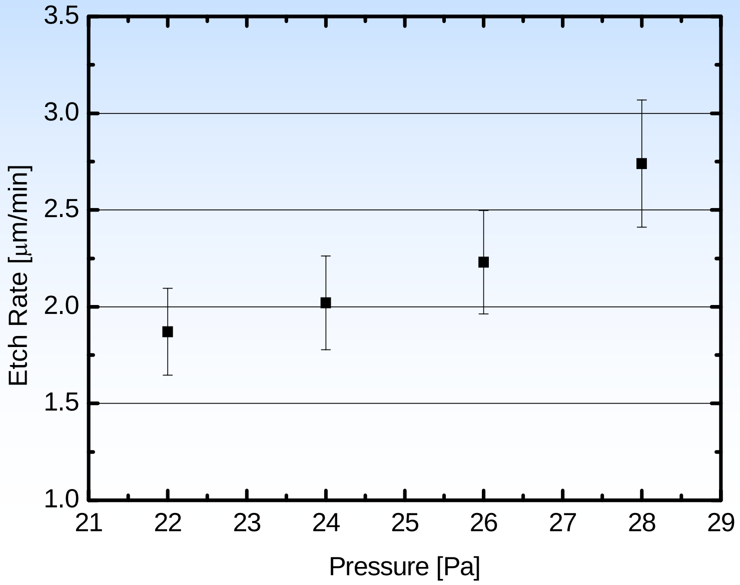


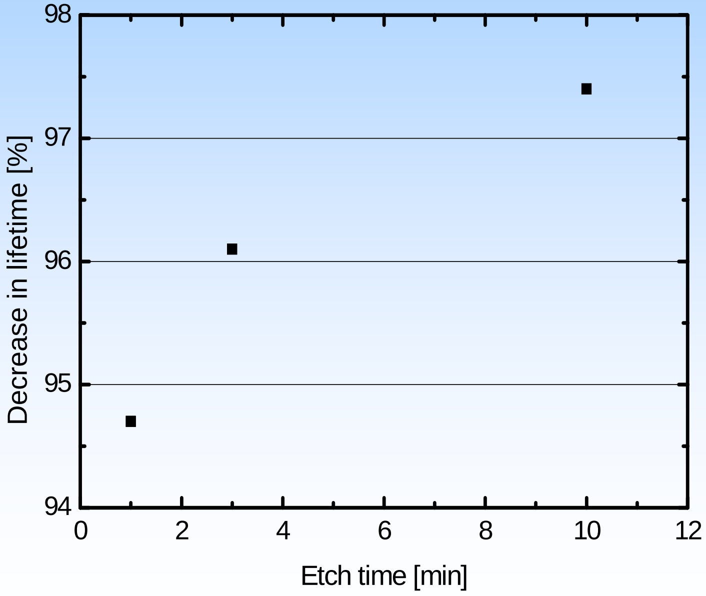
- SiO_2 film etch rate is almost constant:
  - Polymer layer may not completely removed.
- Best uniformity is obtained at low pressure: larger beam diameter

Saw damage layer removal by SF_6 plasma

Plasma induced damage

photoconductance decay measurements





Time dependence of Si etching using ETP technique

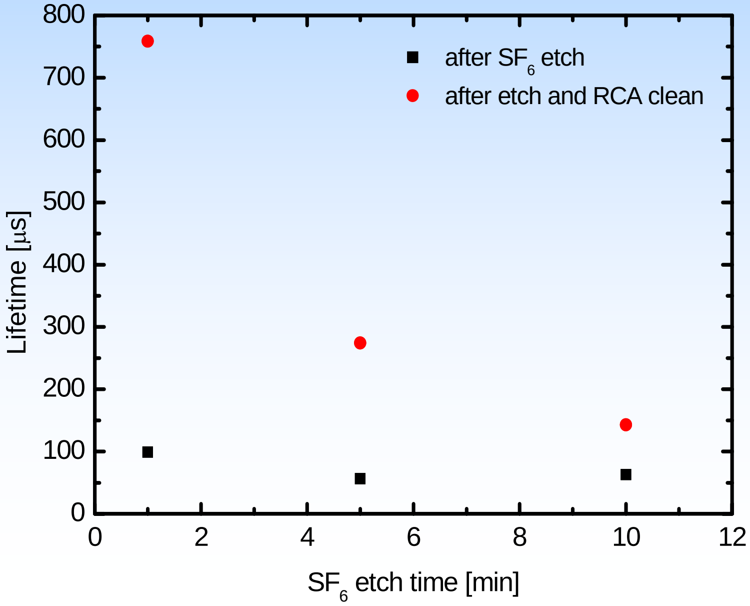
High Si etch rate can be obtained with ETP technique

- The degradation of the lifetime is attributed to the plasma induced damage layer.

Saw damage layer removal by SF_6 plasma

Induced plasma damage layer removal

- Wet chemical back etch (RCA clean) process:
  - Layer of 1 to 2 nm has been etched.
  - Plasma Induced damage is partially removed by
  - more than 90 % of the original lifetime can be recovered when short plasma etching time is applied (~ 2.7 mm Si etched layer),



SiO_2/PSG etching typical results

Plasma etching system	Etching gases used	Etch rate	DC Bias	Reference
RIE system	CHF_3/O_2	17 nm/min (PSG)	340 V	S. Schaefer et al., 1999
MWRIE	CF_4/C_2H_4	~ 30 nm/min (SiO_2) optimum selectivity	~ 300 V	J. Rentsch et al., 2003
ECR-RIE	CF_4/C_2H_4/Ar	37 nm/min (SiO_2)	370 V	K. Roth et al., 2004
PECVD batch reactor	CHF_3/SF_6	~ 3 nm/min (PSG)	RF plasma	A. Nositschka et al., 2003
ETP system	CHF_3/SF_6	~ 40 nm/min (SiO_2) (more than 80 nm/min)	No Bias (With bias)	This work

Conclusions

- Silicon oxide etching using fluorine-containing gases has been demonstrated (for the first time) with the ETP technique.
- High etch rates (> 40 nm/min) have been achieved even in the absence of the biasing sources.
- Plasma parameters have a significant impact on the SiO_2 etch rate.
- Etch rate is almost constant and uniform during the etching process.
- By wet chemical back etch, the induced damage layer can be removed.

Outlook:

Further investigation:

- Determine and optimize of SiO_2/Si etch selectivity.
- Replace wet chemical back etch with dry one (complete dry process)
- Expanding Thermal Plasma for Photovoltaic Applications:
    - Phosphorous silicate glass (PSG) etching
    - Silicon solar cells texturisation.

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