Influence of the acid and alkaline texturization process on basic opto-electronic parameters of the silicon solar cells

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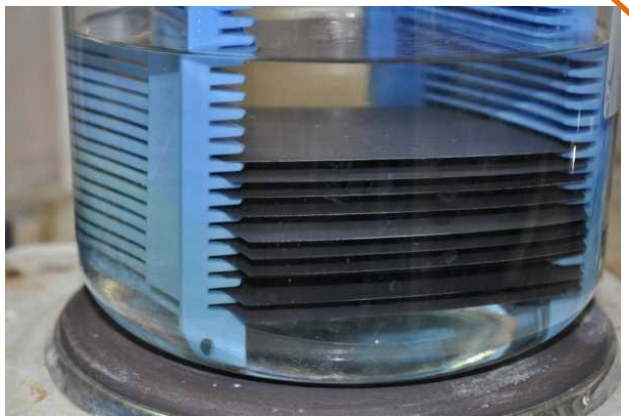
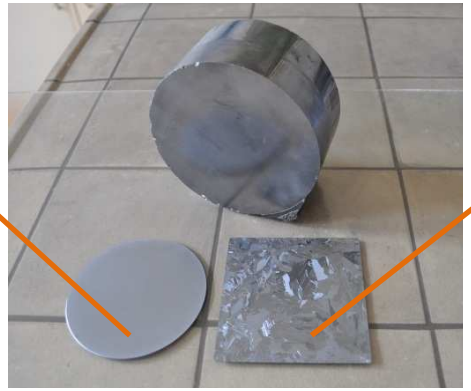
Texturization – the aim of process

Alkaline texturization of monocrystalline silicon

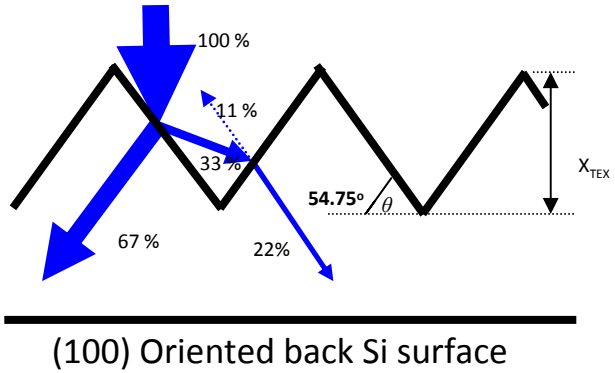




Samples prepared for SEM investigations

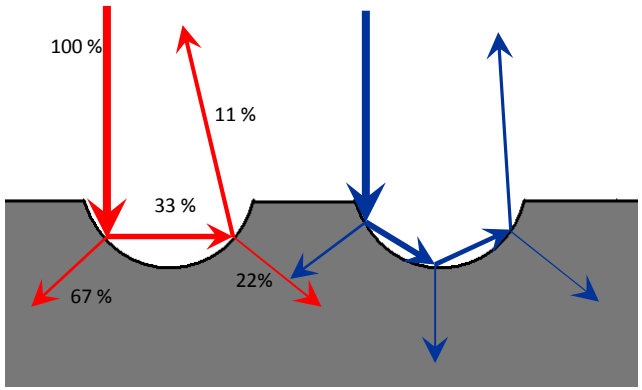
Acid texturization of polycrystalline silicon

Pyramidal structures after alkaline texturization



(100) Oriented back Si surface

Rounded pits structures after acid texturization



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Texturization – the mixture preparation

Alkaline texturization

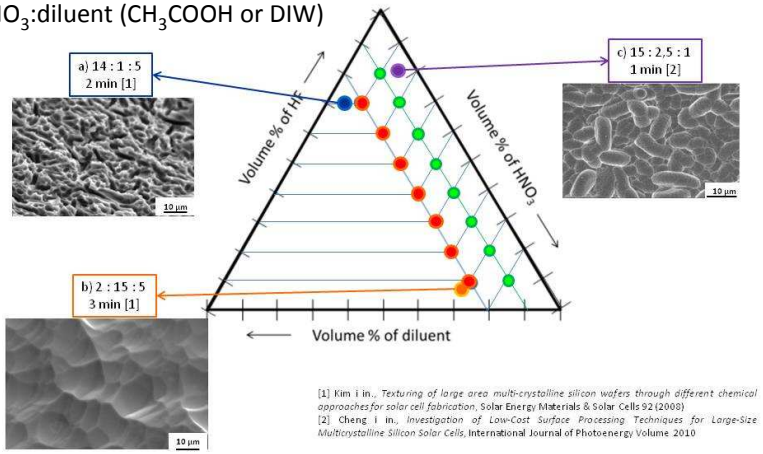
✓Preliminary etching : 30% KOH, 80°C, 3 min
✓KOH:IPA:DIW (1:3:46) 80°C (40 min)
✓KOH:DAA:DIW 94-96°C (10; 15; 17.5; 20; 30; 40 min)
✓KOH:1,2-pentanediol:DIW (1M KOH, 2% alcohol) 80-90°C, 10-40 min, with and without blending)
✓<u>Another cleaning technology :</u>

- 2% HF - 1 min
- $CHCl\text{-}CCl_2$ - rinsing
- $CH_3\text{-}CO\text{-}CH_3$ hot - rinsing
- H_2SO_4:DIW (1:1) - etching
- DIW - rinsing
- HF:DIW (1:10) - etching
- DIW - rinsing

T_bH_2O	= 100 °C
$T_bCH_3CH(OH)CH_3$	= 82 ° C
$T_bCH_3CH(O)CH_2C(CH_3)(OH)CH_3$	= 158 °C
$T_bCH_2(OH)CH(OH)CH_2CH_2CH_3$	= 206 °C

Acid texturization

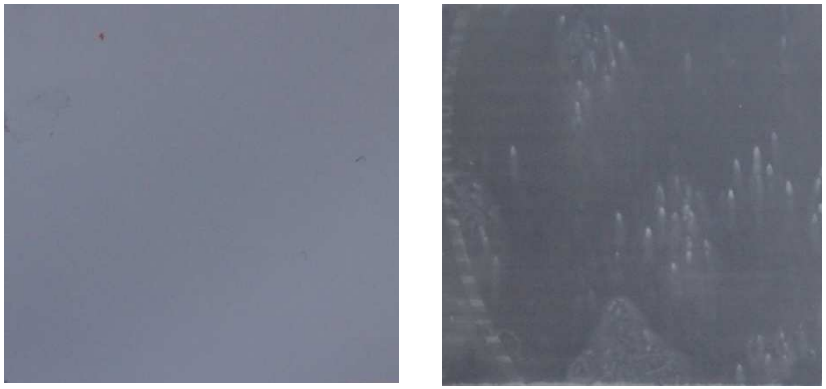
HF:HNO_3:diluent (CH_3COOH or DIW)



[1] Kim i in., *Texturing of large area multi-crystalline silicon wafers through different chemical approaches for solar cell fabrication*, Solar Energy Materials & Solar Cells 92 (2008)
[2] Cheng i in., *Investigation of Low-Cost Surface Processing Techniques for Large-Size Multicrystalline Silicon Solar Cells*, International Journal of Photoenergy Volume 2010

Temperature - ambient
time: 15 - 180 sec

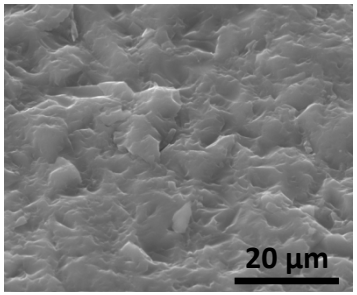
Cz-Si before and after texturization process



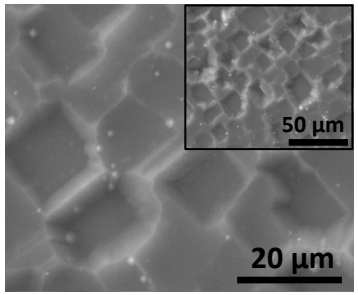
mc-Si before and after texturization process

SEM measurements

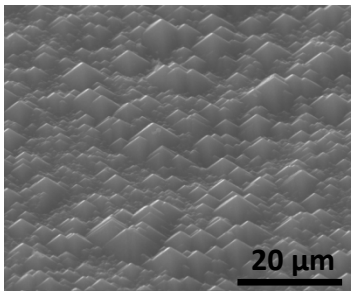
FEI E-SEM XL30; FEI QUANTA 200 3D Dual Beam; Hitachi SU6600



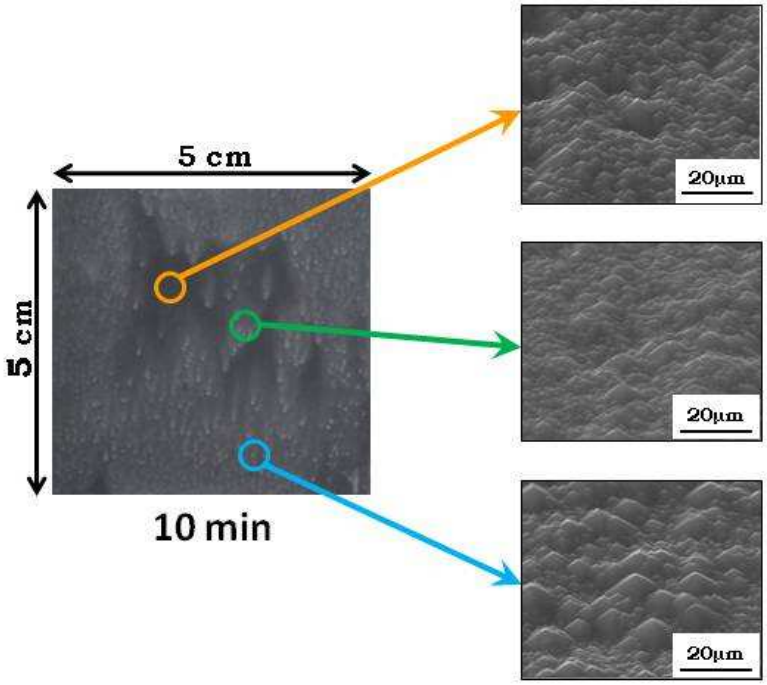
defected surface after diamond saw cutting



surface after KOH preliminary etching



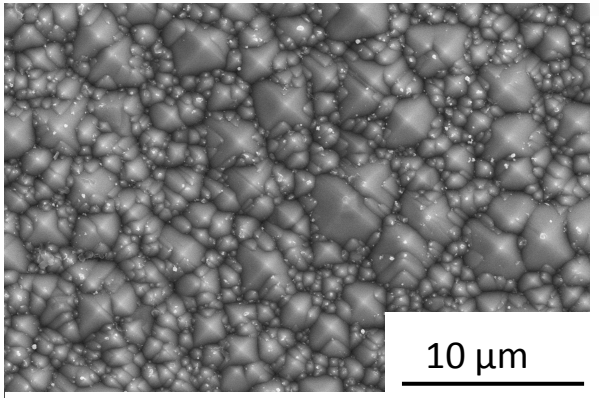
surface after main alkaline texturization

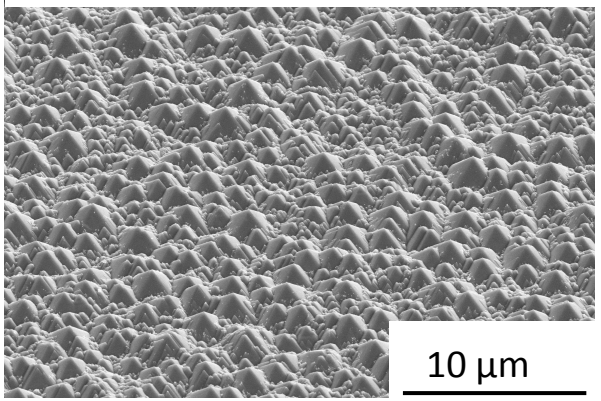


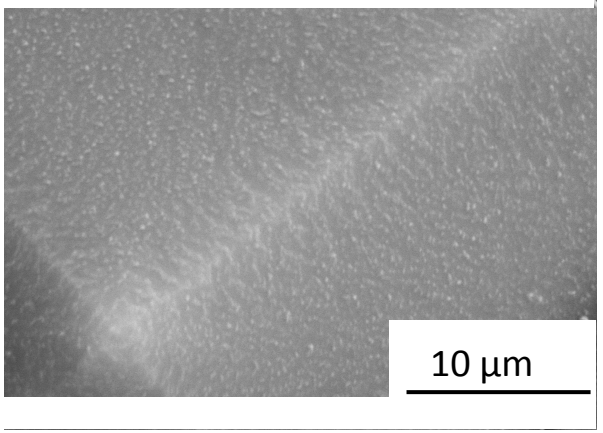
Dark region:
- 2-3 µm
- 5-6 µm

Bright region:
- 1-2 µm
- 5-7 µm

Bright spots region:
- 1-3 µm
- 8-12 µm
- 15 µm

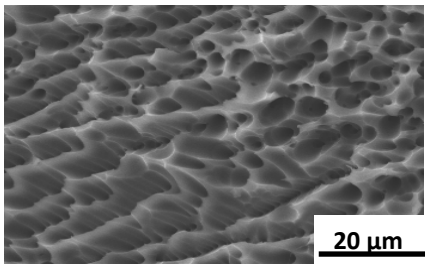




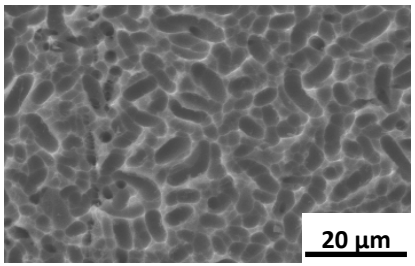


SEM measurements

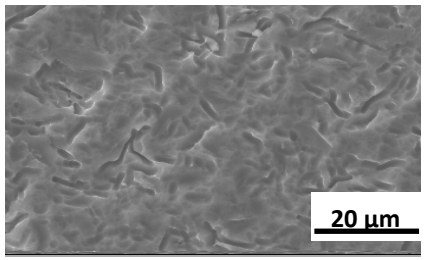
FEI E-SEM XL30; FEI QUANTA 200 3D Dual Beam;



7 HF : 1 HNO_3 : 2 CH_3COOH



7 HF : 1 HNO_3 : 2 H_2O



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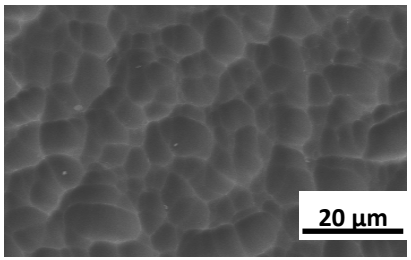

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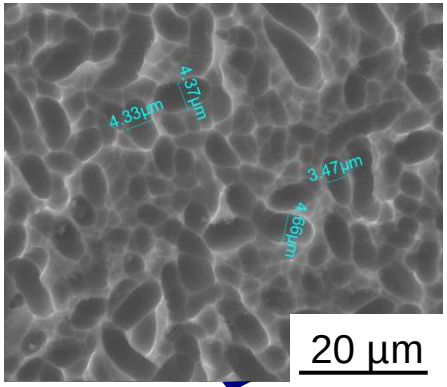

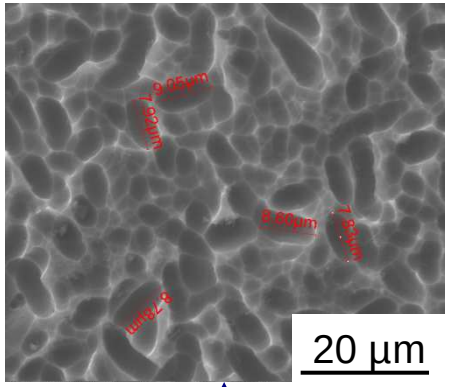

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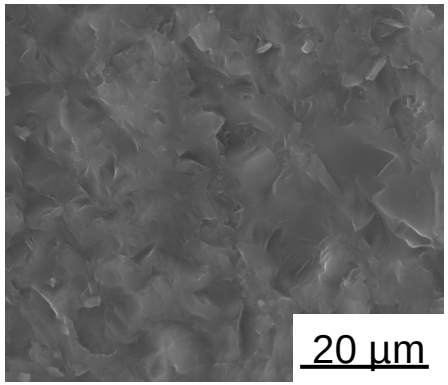
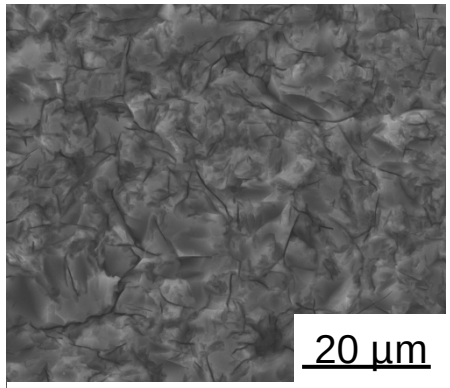
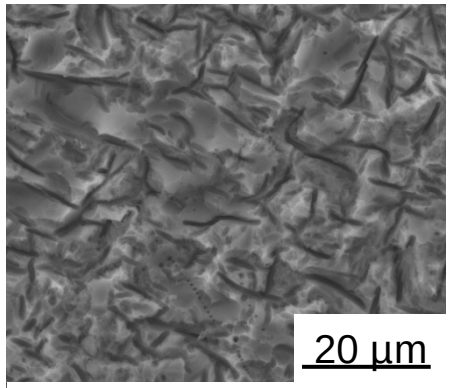


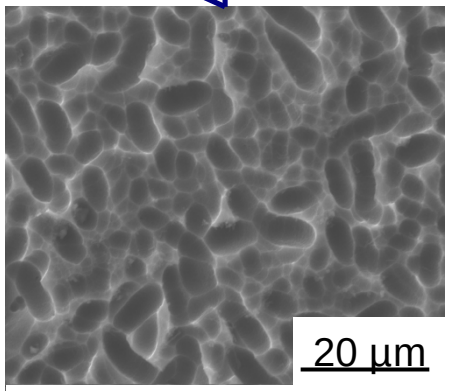
0 sec



30 sec



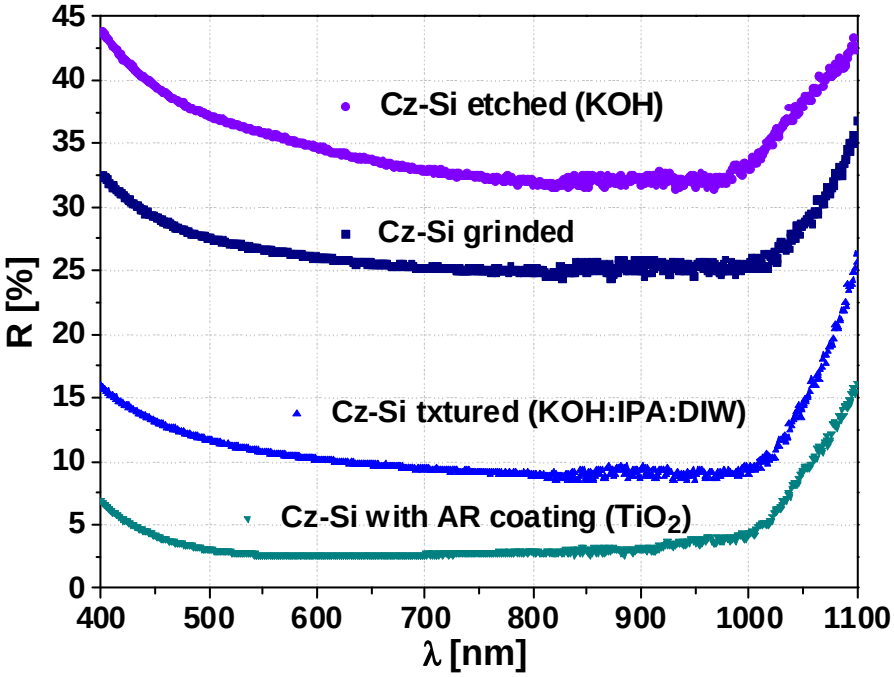
45 sec

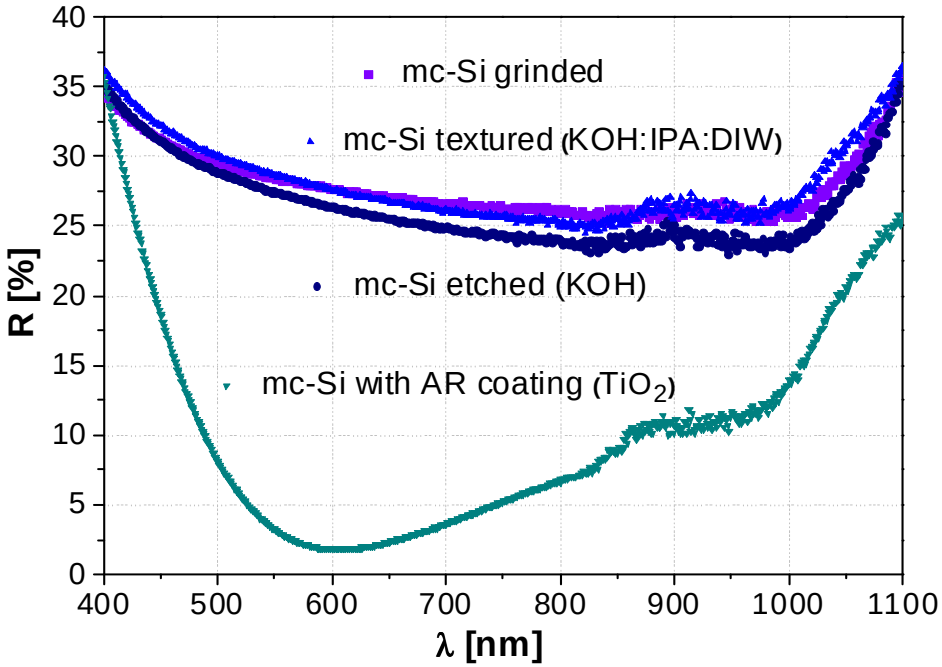


60 sec

Reflectance measurements

Ocean Optics QE 65000 spectrometer with integrated light source DH-2000-BALL

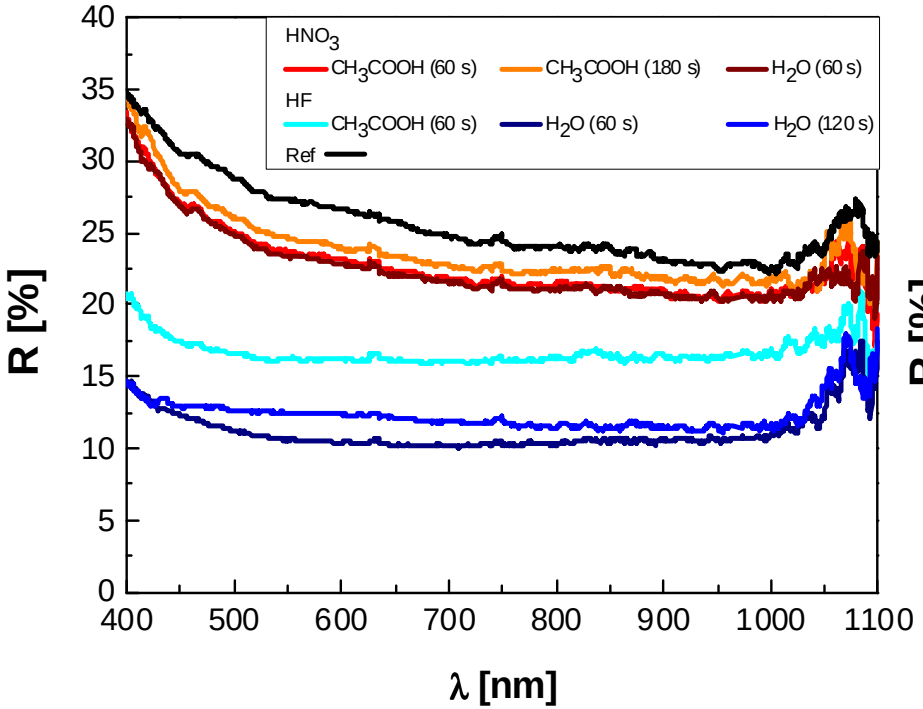


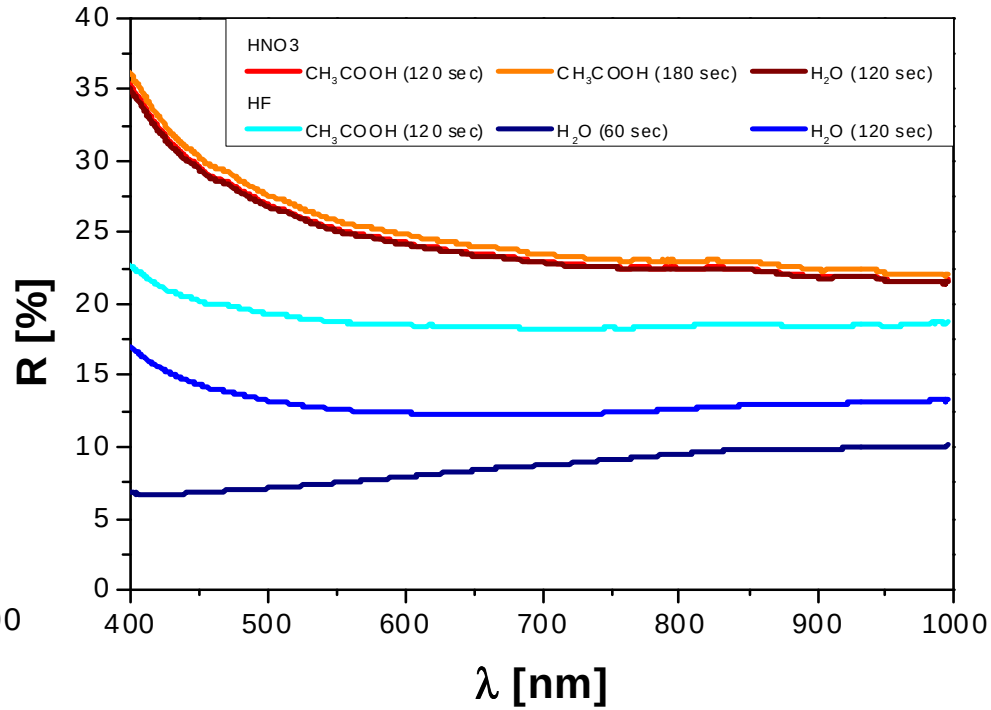


Texturization in alkaline solutions reduces the reflectance of monocrystalline silicon up to 10 % but is ineffective for polycrystalline silicon – there is no significant reflectance reduction after texturization process.

Reflectance measurements

Ocean Optics QE 65000 spectrometer with integrated light source DH-2000-BALL



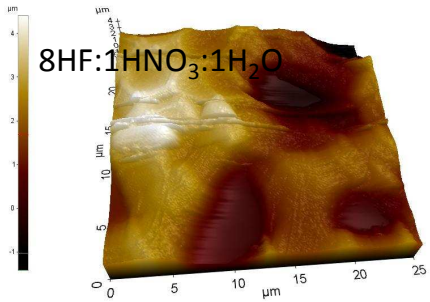


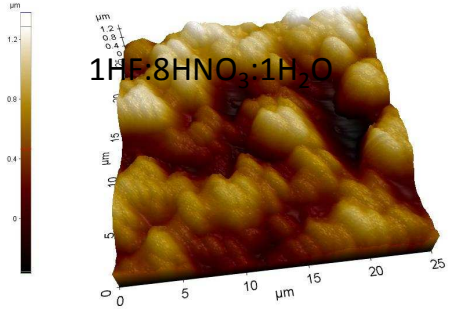
Texturization in acid solutions reduces the reflectance of polycrystalline silicon up to 10 % in mixtures with high HF content with deionized water as a diluent. Additionally the shortest process time (60 seconds) was the best one. This is due to the larger surface roughness after wafers texturization in high HF content solution as shown by the AFM investigations in the following slide.

AFM, profilometer measurements

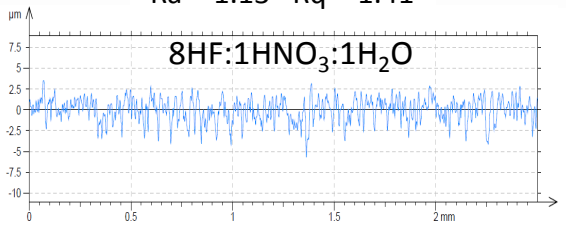
AFM: Park Systems XE-100

Profilometer: Taylor Hobson Surtronic 25

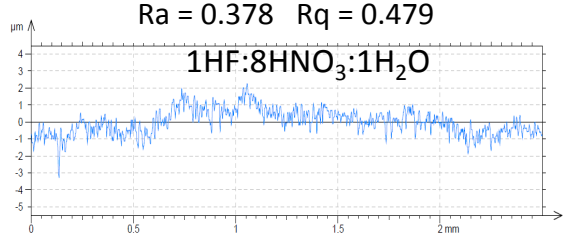




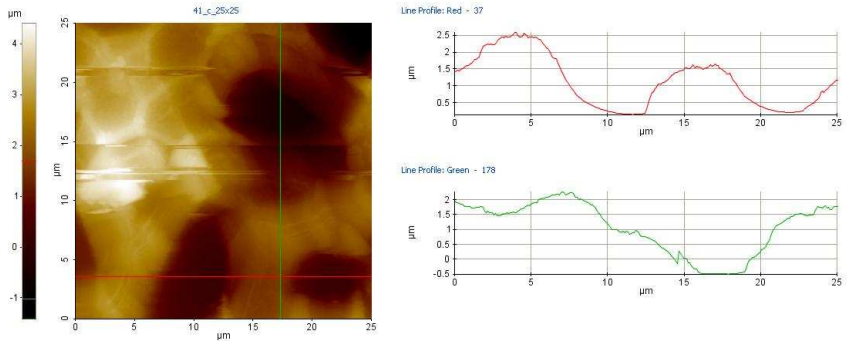
Ra = 1.13 Rq = 1.41

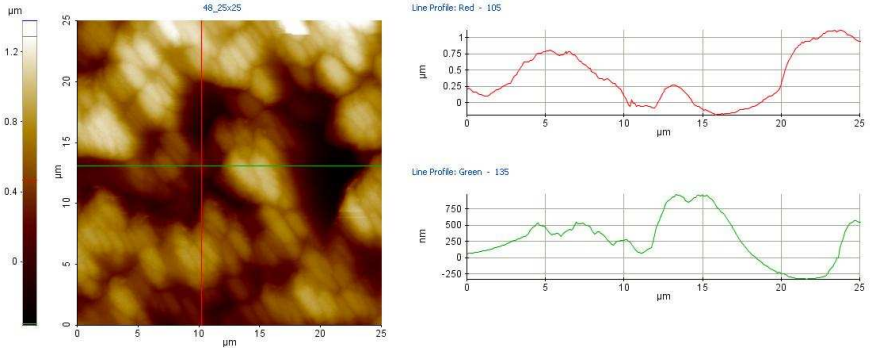


Ra = 0.378 Rq = 0.479



Profilometer investigations shows larger roughness for texturing in high HF content solutions.





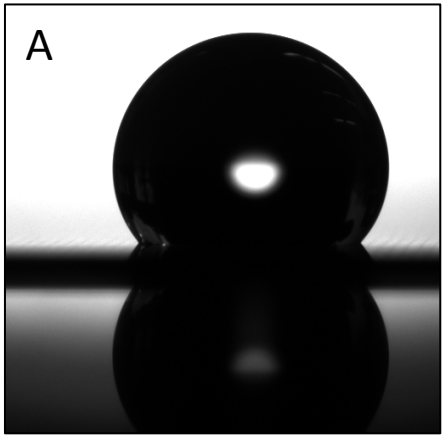
Line	Min [µm]	Max [µm]	Mid [µm]	Mean [µm]	Rq [µm]	Ra [µm]
Red	0.136	2.584	1.360	1.117	0.772	0.674
Green	-0.510	2.263	0.877	1.042	0.872	0.759

Line	Min [µm]	Max [µm]	Mid [µm]	Mean [µm]	Rq [µm]	Ra [µm]
Red	-0.189	1.112	0.461	0.365	0.399	0.350
Green	-0.330	0.974	0.322	0.281	0.362	0.291

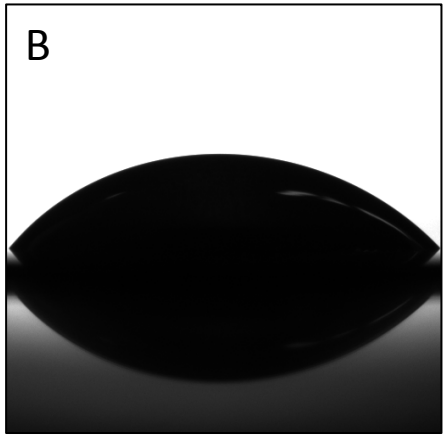
More precise from profilometer studies are AFM investigations. Again the larger roughness of texturing wafers in the high HF content solutions is observed.

Wettability measurements

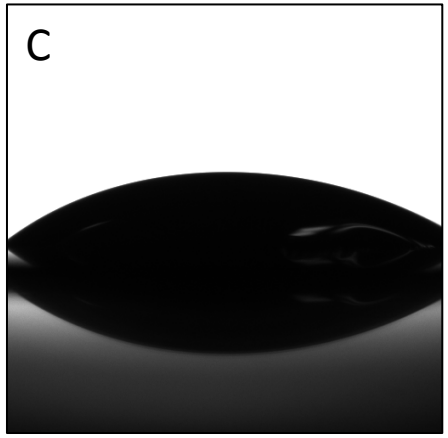
Attension optical tensiometer Theta Lite



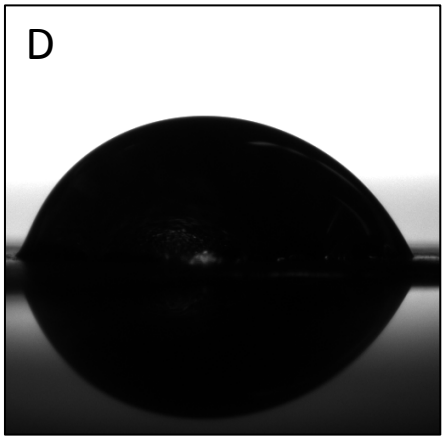
$8HF:1HNO_3:1H_2O$



$1HF:8HNO_3:1H_2O$



$1HF:8HNO_3:1CH_3COOH$



$8HF:1HNO_3:1CH_3COOH$

Sample number	Mean Contact angle [degrees]	Standard deviation [degrees]	Mean Volume [microl]	Standard deviation [microl]
A	134,84	1,39	13,41	0,11
B	46,43	2,83	16,73	10,70
C	85,74	16,63	17,68	11,43
D	38,39	3,24	9,07	1,69

Wafers texturing in high HF content solutions with deionized water as a diluent shows hydrophobic properties. Therefore it is necessary to rinse the wafers with isopropyl alcohol at elevated temperatures.

Solar cells manufacturing process:

- p-n junction formation by diffusion from $POCl_3$ as a source at temperature 850 °C for 25 min (20 min pre-diffusion and 5 min re-diffusion) resulting in the surface resistance R_s = 53 Ω/□
- edge separation (CP-4 mixture: 3 HF : 5 HNO_3 : 3 CH_3COOH in volume ratio)
- phosphorous silica glass PSG removal using 10% HF
- passivation by thermal oxidation at 800 °C for 10 min
- antireflective coating deposition of TiO_x by CVD method
- screen-printing ohmic contacts using Ag and Al pastes (Du Pont PV 159, PV 381)
- firing in III-zone belt IR furnace



Light current-voltage (LIV) characteristics examination:

LIV simulator calibrated by the reference cell measured at the Institut für Solarenergieforshung GmbH Hameln/Emmerthal (AM 1.5, 1000 W/m^2, 25 °C)

Type of silicon	Type of texturing mixture	Temperature and time	I_{SC} [mA]	V_{OC} [mV]	P_m [mW]	FF [%]	Eff [%}
Cz-Si	KOH:DAA:DIW 1 :3 : 46	94-96 ℃ 10 min	845.7	592.6	385.9	77.0	15.4
mc-Si	HF:HNO_3:DIW 7 : 1 : 2	ambient 60 sec	769.2	583.3	340.4	75.9	13.6

I_{sc} – short circuit current, V_{oc} – open circuit voltage, P_m – maximum power, *FF* – fill factor, E_{ff} – photovoltaic conversion efficiency

Future investigations:

✓Upcoming researches:

•Silicon defects designation for raw material and silicon wafers after texturization process (cooperation with Institute of Physics, Wrocław University of Technology)

•Carrier lifetime (for the characterization of a good texture)

•Influence of texturization process temperature on opto-electronic parameters of silicon wafers and solar cells investigations (temperature lowering, cooling medium)

✓Further researches:

•Determine the area of dislocation etching on the concentration triangle in order to avoid this type of solution (wafers fragility)

•Determination of the formation of porous silicon

•Surface development investigations: mercury porosimetry or nitrogen sorption (cooperation with Faculty of Materials Engineering and Ceramics, AGH University of Technology)

•Determination of recombination centers by LBIC (Light Beam Inducted Current)

•Determination of IQE (Internal Quantum Efficiency)