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# Lifetime of ALD $\text{Al}_2\text{O}_3$ Passivated Black Silicon Nanostructured for Photovoltaic Applications

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## Abstract

Black silicon nano-structures provide significant reduction of silicon surface reflection due to highly corrugated nano-structures with excellent light trapping properties. However, most recent RIE techniques for black silicon nano-structuring have one very important limitation for PV applications – high surface recombination velocity due to intensive plasma ion bombardment of the silicon surface. In an attempt to optimize black silicon for PV applications we develop a mask-less one step reactive ion nano-structuring of silicon with low ion surface damage with reflectance below 0.5%. For passivation purposes we used 37 nm ALD  $\text{Al}_2\text{O}_3$  films and conducted lifetime measurements and found 1220  $\mu\text{s}$  and to 4170  $\mu\text{s}$ , respectively, for p- and n-type CZ silicon wafers. Such results are promising results to introduce for black silicon RIE nano-structuring in solar cell process flow

## Mask-less Black Silicon Nano-Structuring With RIE

Reactive Ion Etching Process Parameters	Values
Etch Time, min	16 min
Pressure, mTorr	38
O <sub>2</sub> flow, sccm	100
SF <sub>6</sub> flow, sccm	70
Coil Power, W	3000
Platen Power, W	10
Chiller temperature, C	-20
Etch rate, nm/min	98
Nanostructuring rate, nm/min	30

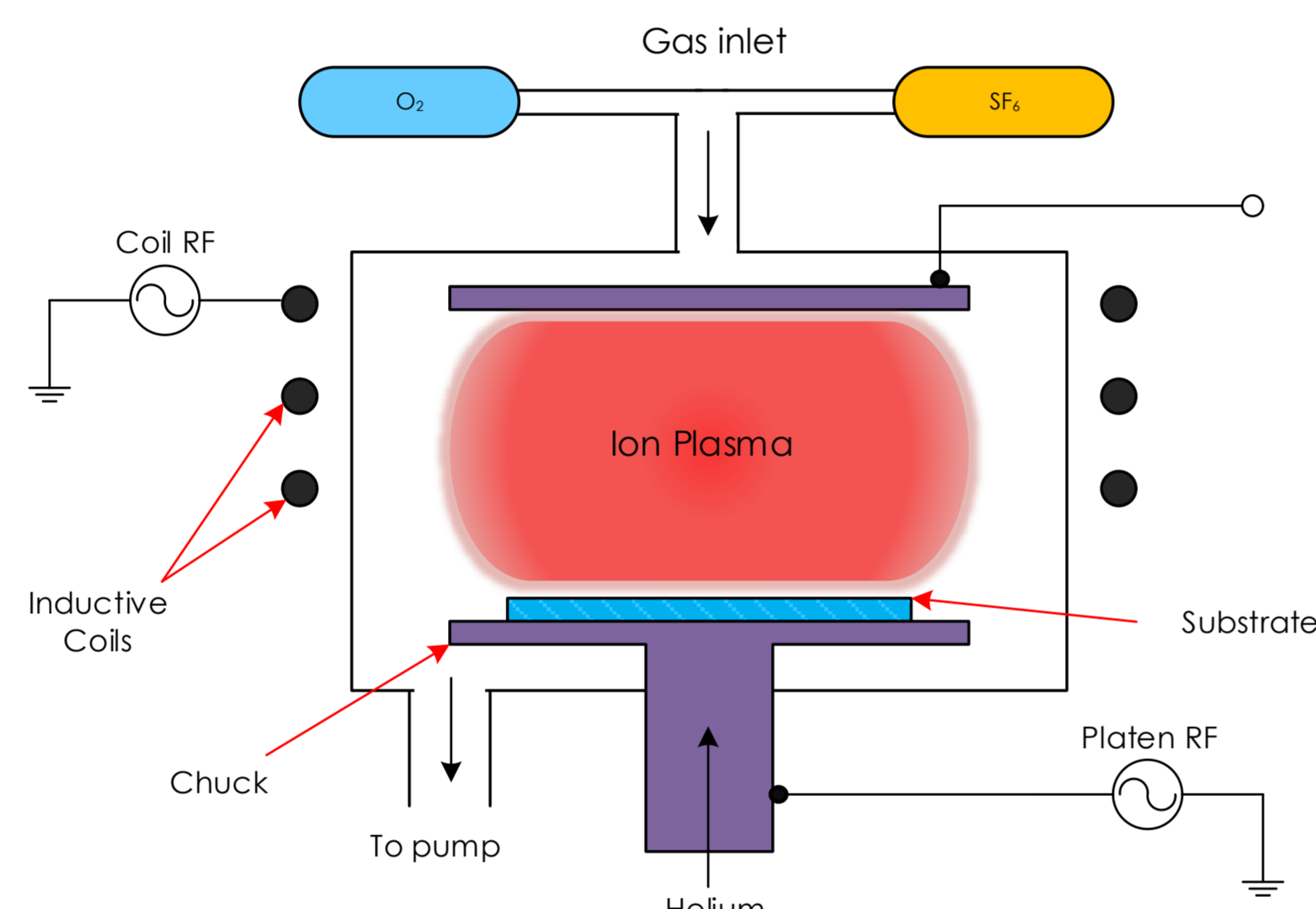


Fig.1. Schematic of inductive coupled plasma system used for RIE

### Black Silicon Nano-Structuring Process

- A wafer is loaded in to the ICP RIE chamber and cooled to -20°C.
- SF<sub>6</sub> gas is supplied to the chamber and fluorine radicals rapidly attack the silicon and destroy native oxide on top forming volatile SiF<sub>4</sub>.
- In the next step oxygen is supplied to the chamber. Oxygen radicals form silicon-oxyfluorine SiF<sub>4</sub>+O\*→SiO<sub>x</sub>F<sub>y</sub> at low temperature (-20°C). SiO<sub>x</sub>F<sub>y</sub> acts as an etch stop for F\*. On horizontal planes, this layers passivates is bombarded by ions from plasma while on the vertical sidewalls the ion bombardment is weaker due to directionality of the plasma ions and the sidewalls therefore remain protected from chemical etching by fluorine radical [1-2].

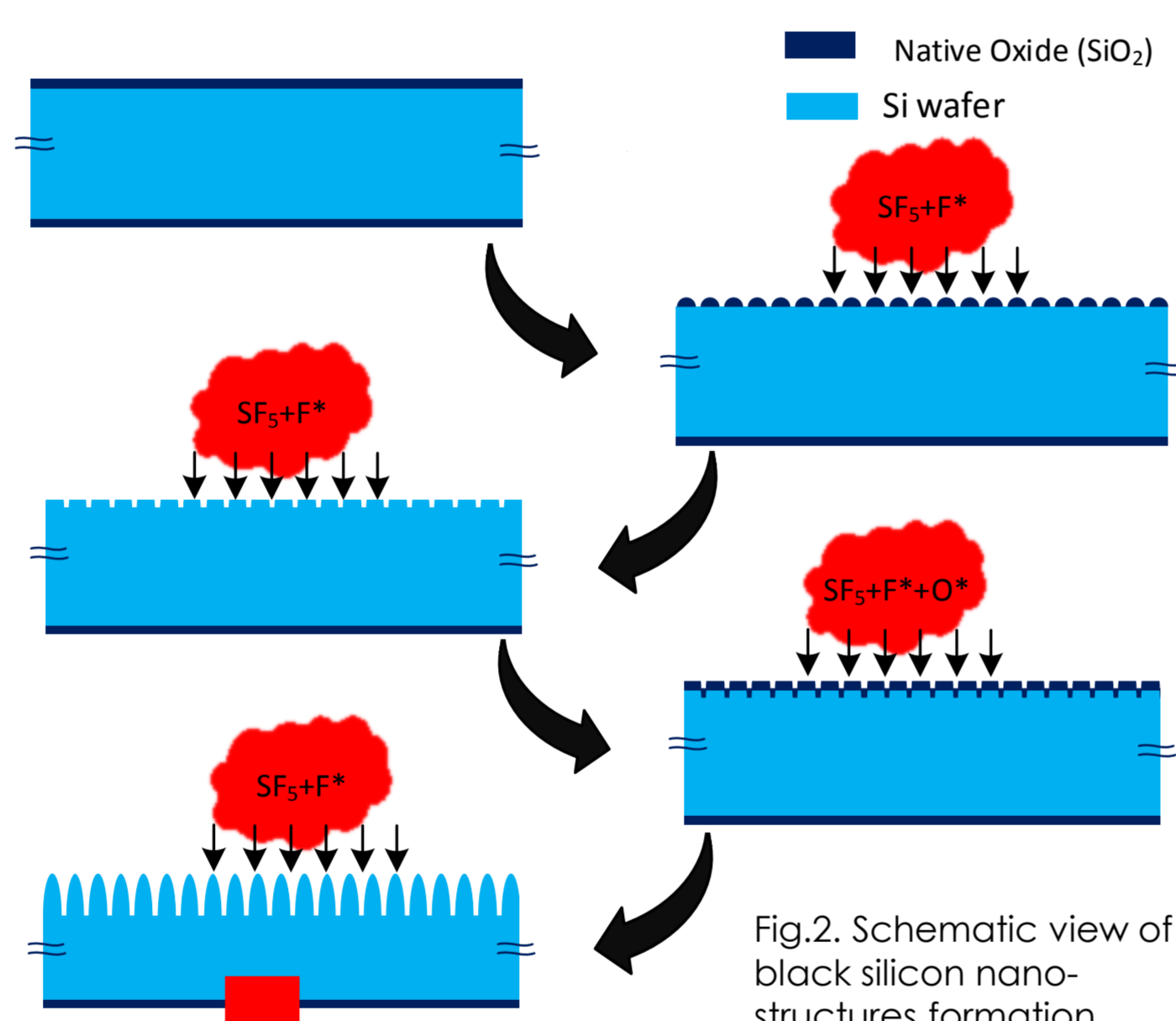
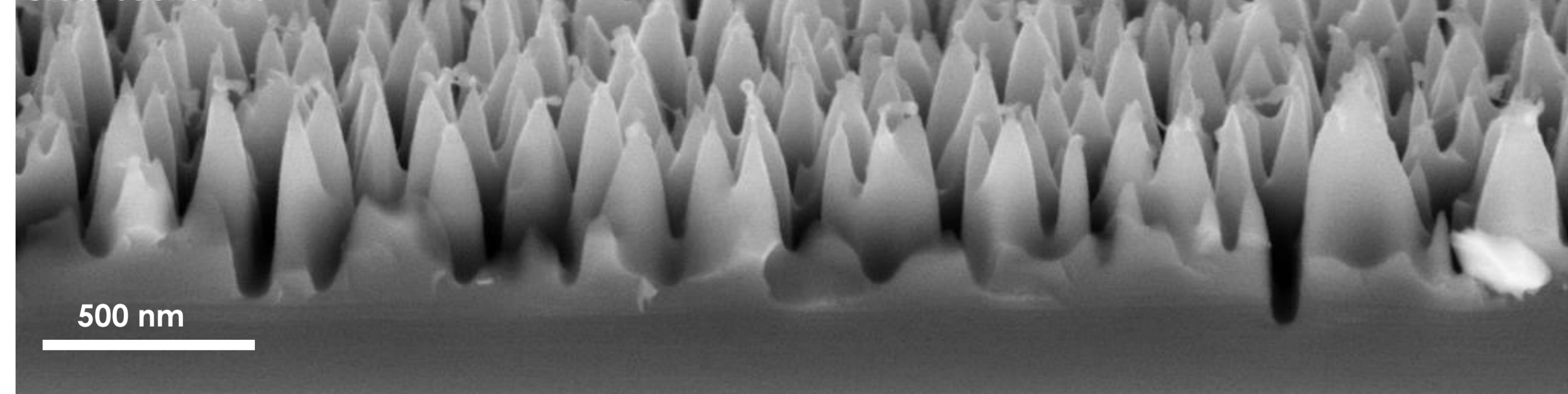


Fig.2. Schematic view of black silicon nano-structures formation

### Cross-section view



### Principles for low ion damage black silicon nano-structures

- Aspect ration of nano-structures was controlled via the low gas pressure (38 mTorr) which determined the directionality of the ions and the physical etching components by limiting the mean free path of the plasma species.
- High coil power (3000 W) is used to create homogeneous plasma with ions and maintain stable high etch rate.
- Low platen power (10 W) limits kinetic energy of ions, directed towards the substrate surface.
- Average flow of SF<sub>6</sub> gas (70 sccm) allows to keep stable Si etch rate.
- High O<sub>2</sub> flow (100 sccm) allows to passivate Si surface and lower etch rate.

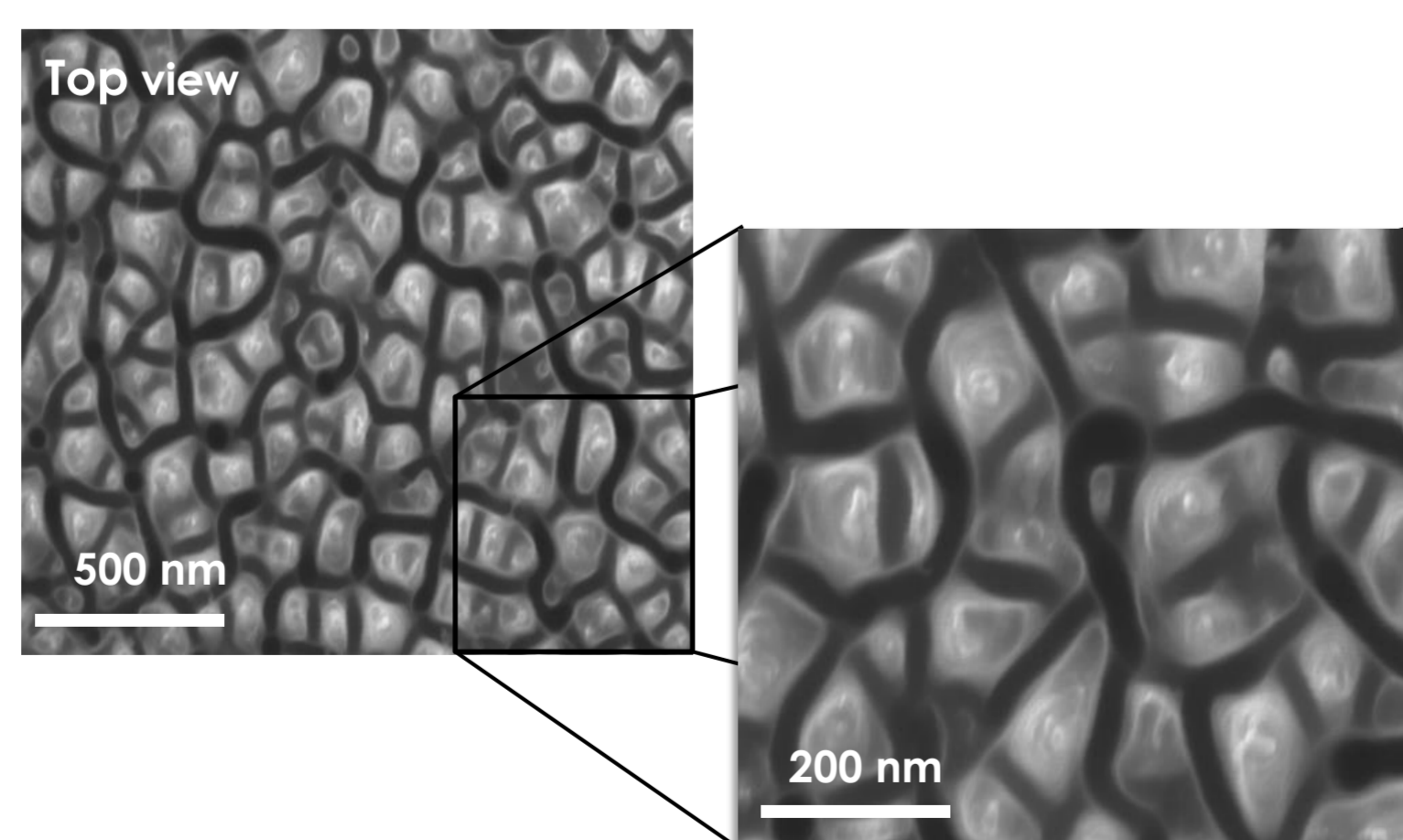


Fig. 3. SEM images of the black silicon nano-structure topology processed with plasma assisted mask-less RIE

## Passivation Of Black Silicon With ALD $\text{Al}_2\text{O}_3$

### ALD $\text{Al}_2\text{O}_3$ Passivation Process

After RIE all samples were cleaned in standard RCA cleaning solutions. Subsequently, wafers were coated with 380 cycles of ALD  $\text{Al}_2\text{O}_3$  synthesized from trimethylaluminum (TMA) and H<sub>2</sub>O with pulse time 0.1 sec and purge time 4 sec for 1 cycle in ALD Picosun R200. For reference purposes two polished wafers of different type were also included in ALD  $\text{Al}_2\text{O}_3$  passivation procedure. The passivation layers were activated by post-deposition ALD in-situ annealing in N<sub>2</sub> ambient at 375-390 °C for 30 min. The resulting  $\text{Al}_2\text{O}_3$  thickness of 37 nm was measured from polished reference samples with spectroscopic ellipsometry.

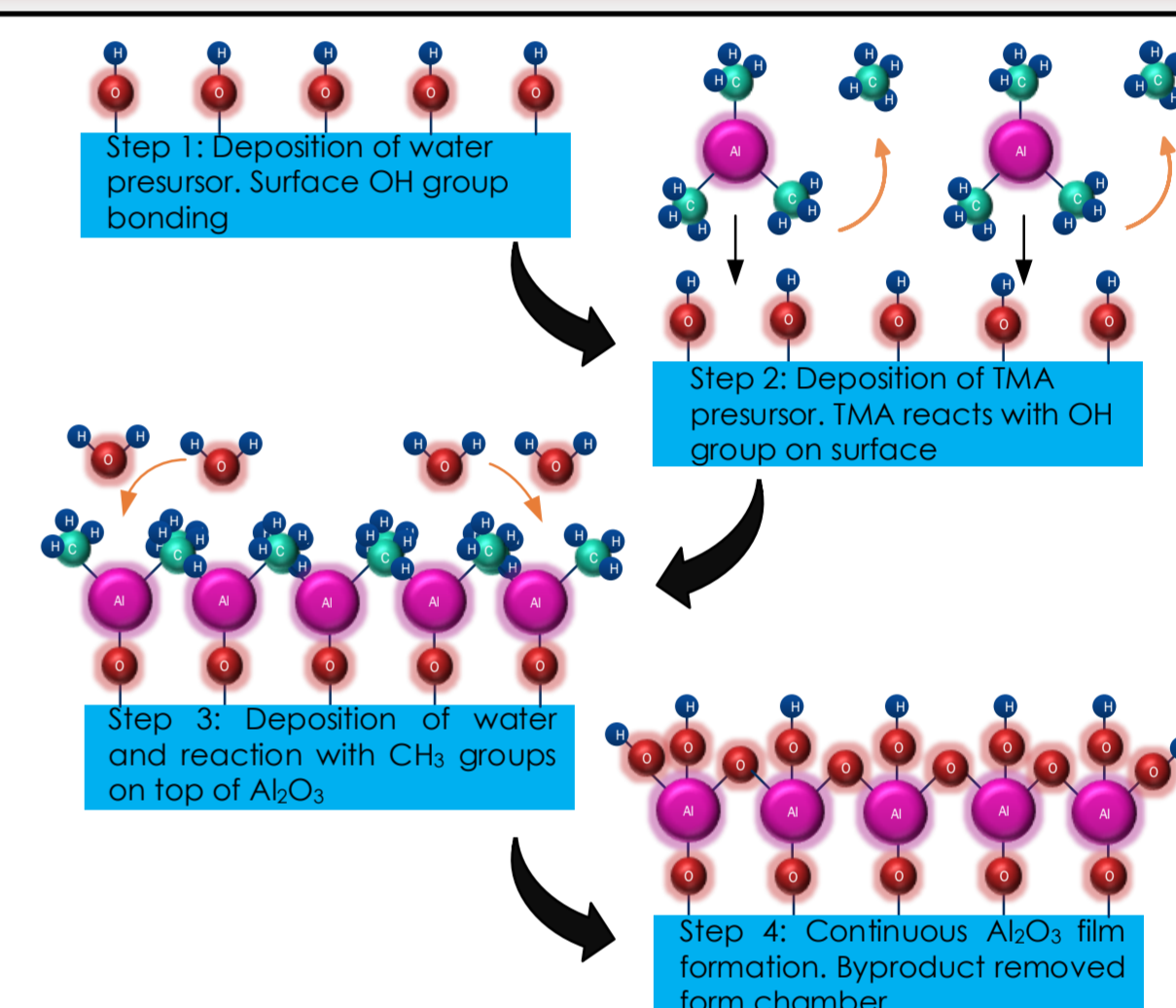


Fig.4 Schematic view of ALD  $\text{Al}_2\text{O}_3$  (1 cycle)

### Minority Carrier Lifetime Measurements

We used microwave detected photoconductivity method (MDP) and MDPmap setup from Freiberg Instruments for measurements of effective minority carrier lifetime on p- and n-type polished and nano-textured wafer samples.

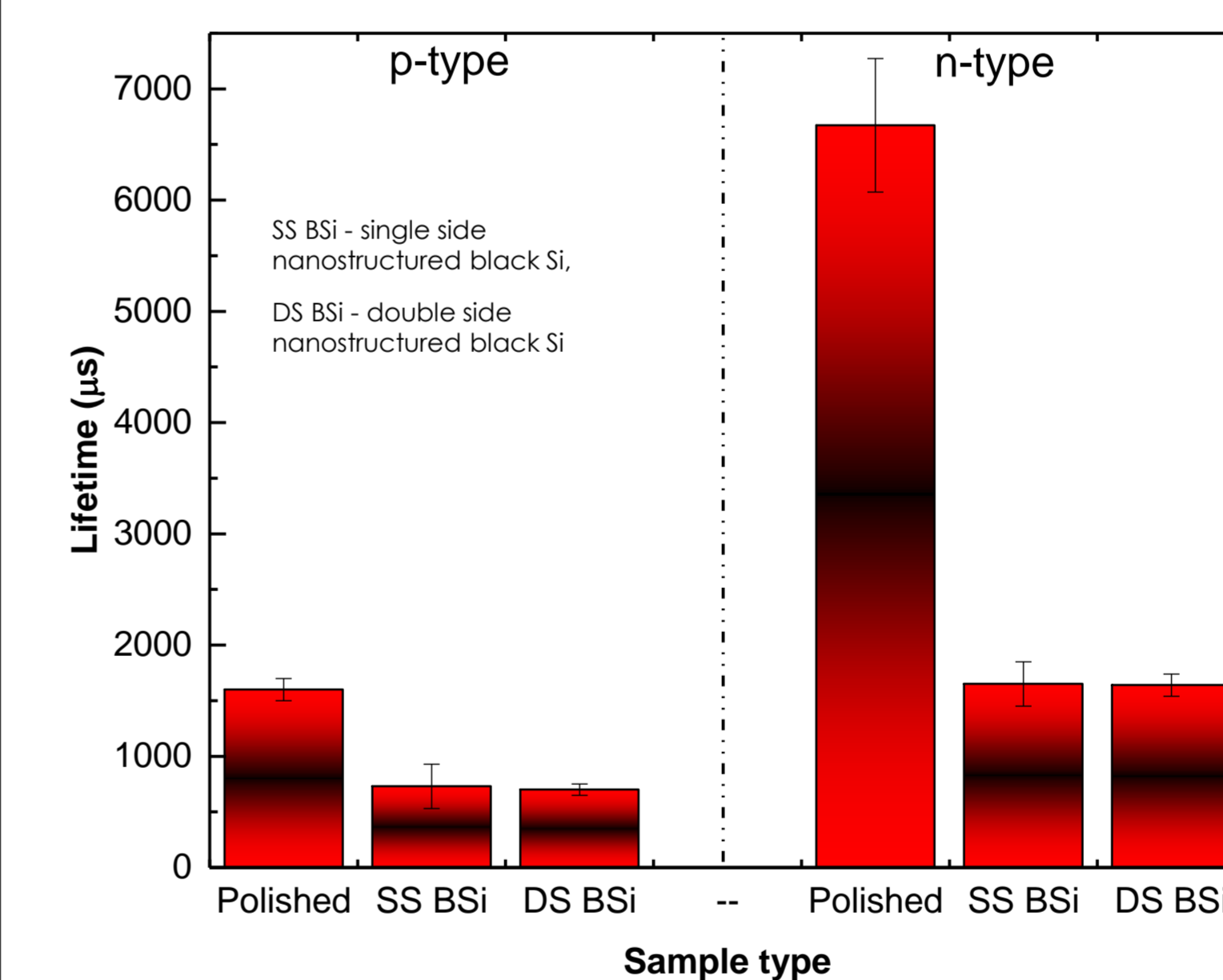


Fig. 5 Comparative graph of average lifetime wafer mapping values with standard deviation for p and n type silicon samples with polished, single side nano-structured and double side nano-structured black silicon, passivated with ALD  $\text{Al}_2\text{O}_3$  35 nm film

Single side and double side nano-structured samples have almost equal lifetime and therefore we can conclude that only damage surface controls surface recombination velocity and the lifetime is totally dependable on surface properties of textured area.

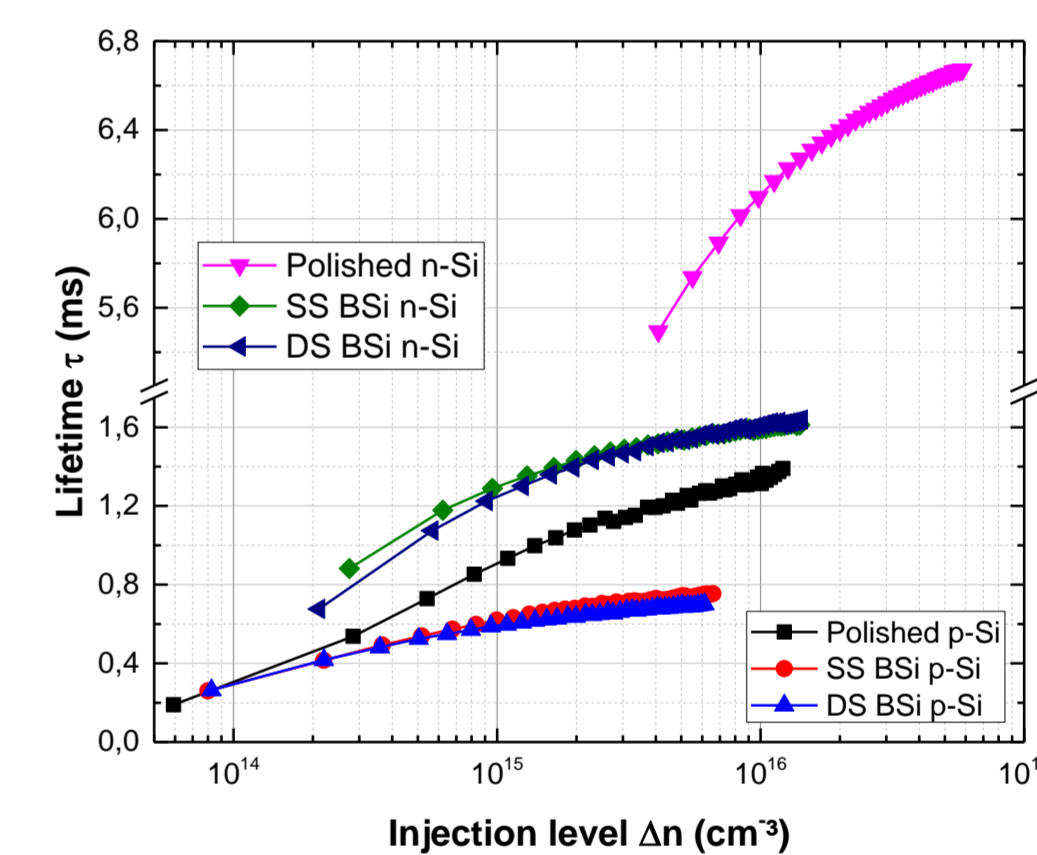


Fig. 6 Effective carrier lifetime vs. injection level

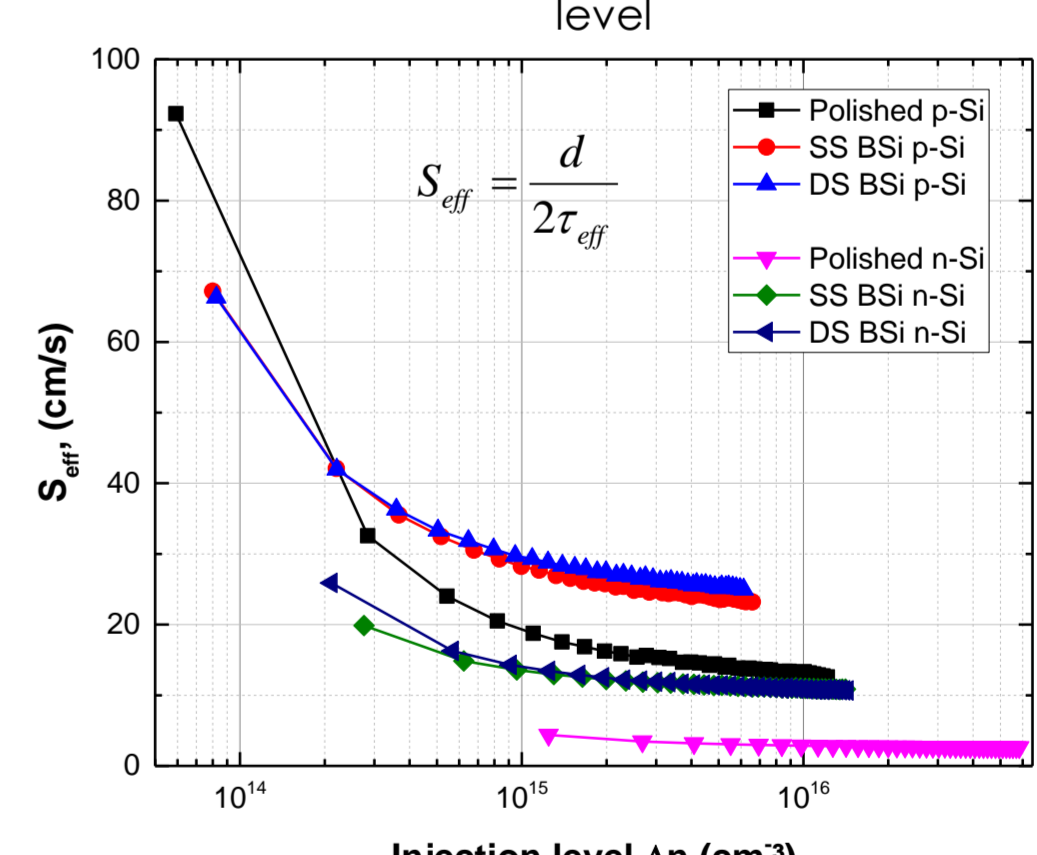


Fig. 7 Surface recombination velocity vs. injection level

## Optical Properties Of Black Silicon

Reflectivity of polished silicon wafer is round 30% while black silicon has in average reflectance below 0.5% at normal incidence.

Increased reflectance of black silicon above 1000 nm is due to silicon transparency in higher range and detection of reflected signal from the white background

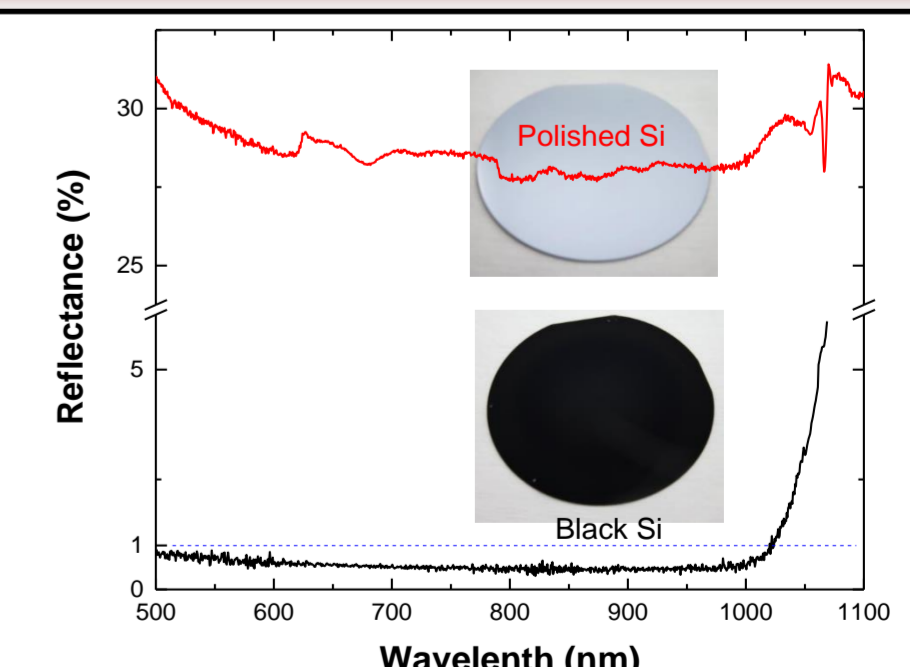


Fig. 8 Experimental reflectance spectra of polished and black silicon without  $\text{Al}_2\text{O}_3$  coating

## Future Work

Further optimization of black silicon surface properties and fabrication of solar cells based in these structures

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