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Lifetime of ALD Al_2O_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 Al_2O_3 films and conducted lifetime measurements and found 1220 μs and to 4170 μs, 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
O2 flow, sccm	100
SF6 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

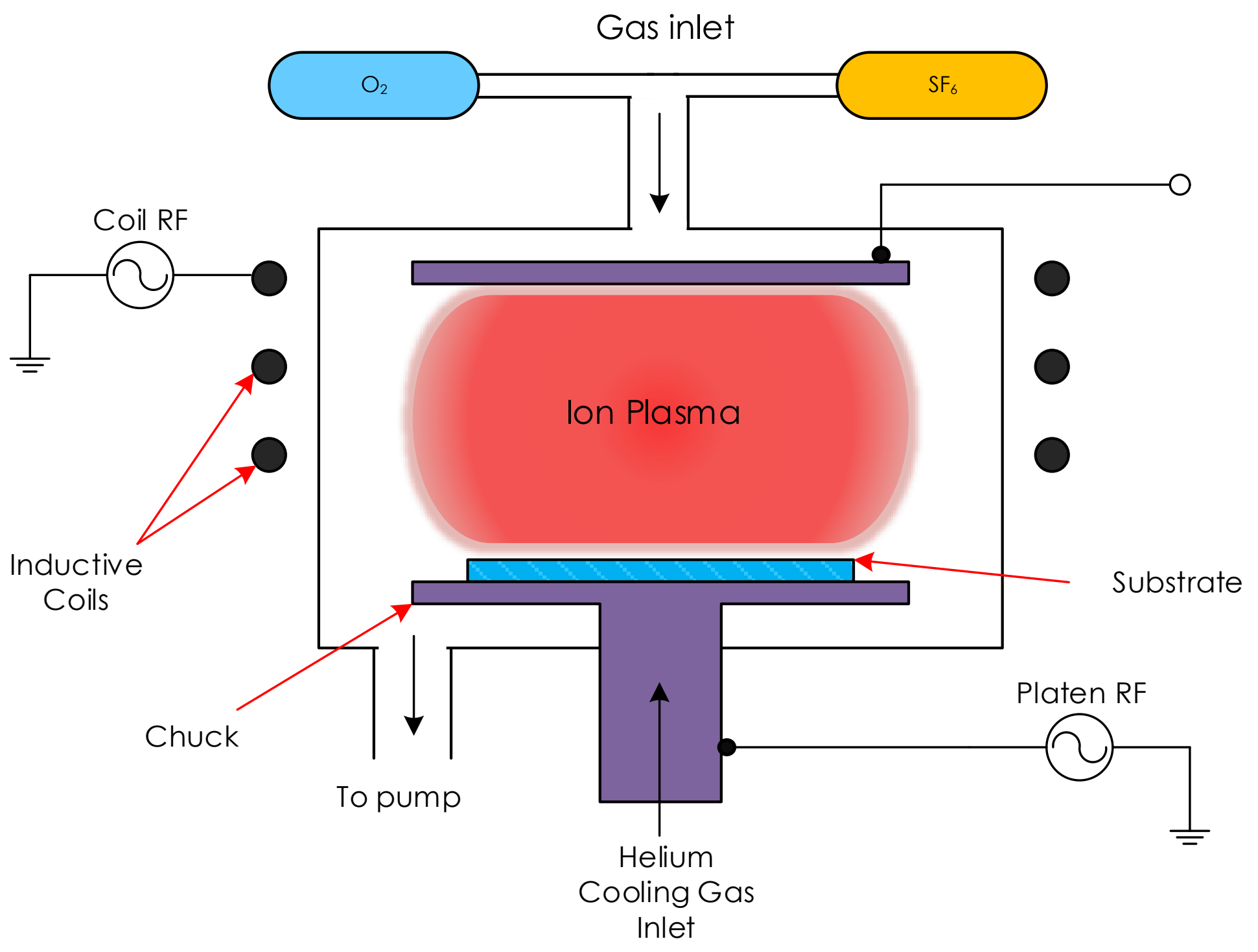


Fig.1. Schematic of inductive coupled plasma system used for RIE

Black Silicon Nano-Structuring Process

- A wafer is loaded in to the ICP RIE chamber and cooled to -20°C.
- SF_6 gas is supplied to the chamber and fluorine radicals rapidly attack the silicon and destroy native oxide on top forming volatile SiF_4.
- In the next step oxygen is supplied to the chamber. Oxygen radicals form silicon-oxyfluorine SiF_4+O*=SiO_xF_y at low temperature (-20°C). SiO_xF_y 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].

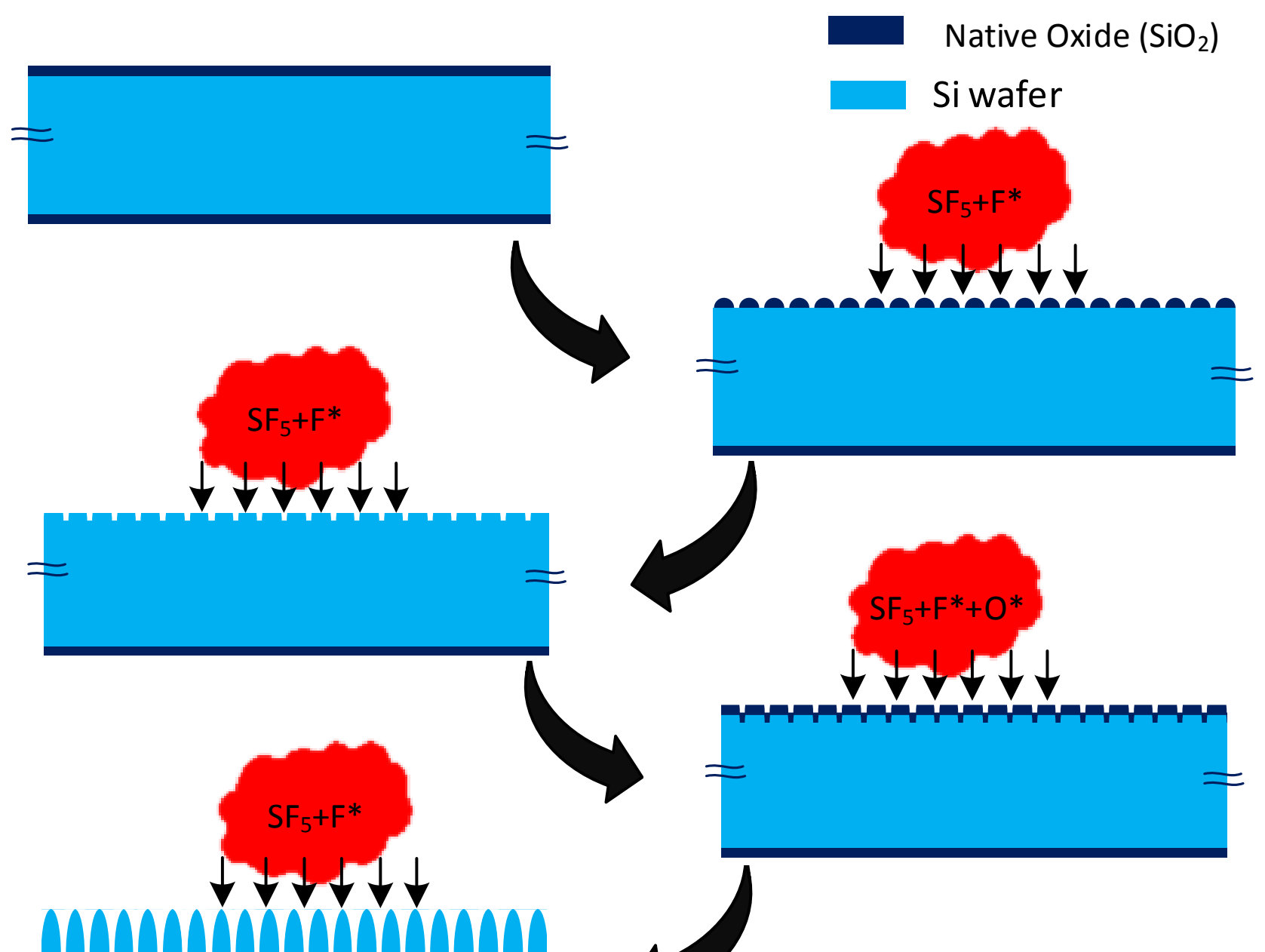
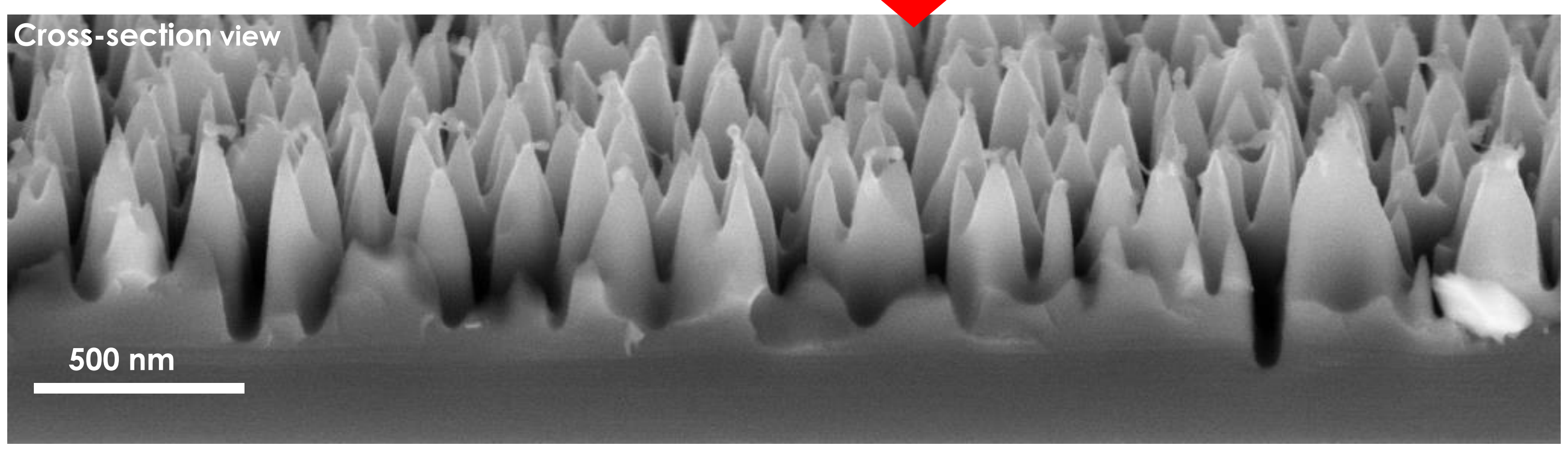


Fig.2. Schematic view of black silicon nano-structures formation



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_6 gas (70 sccm) allows to keep stable Si etch rate.**
- **High O_2 flow (100 sccm) allows to passivate Si surface and lower etch rate.**

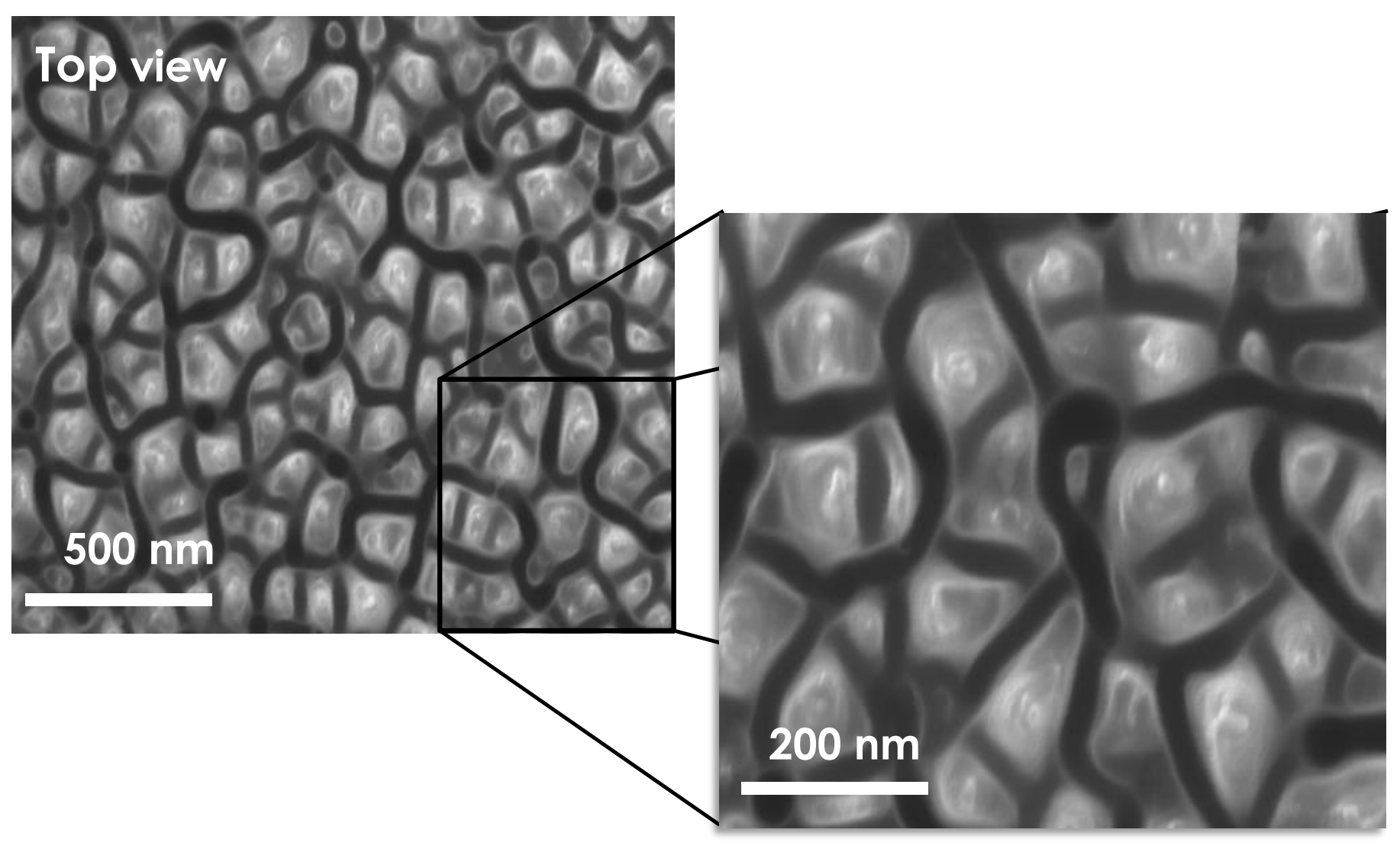
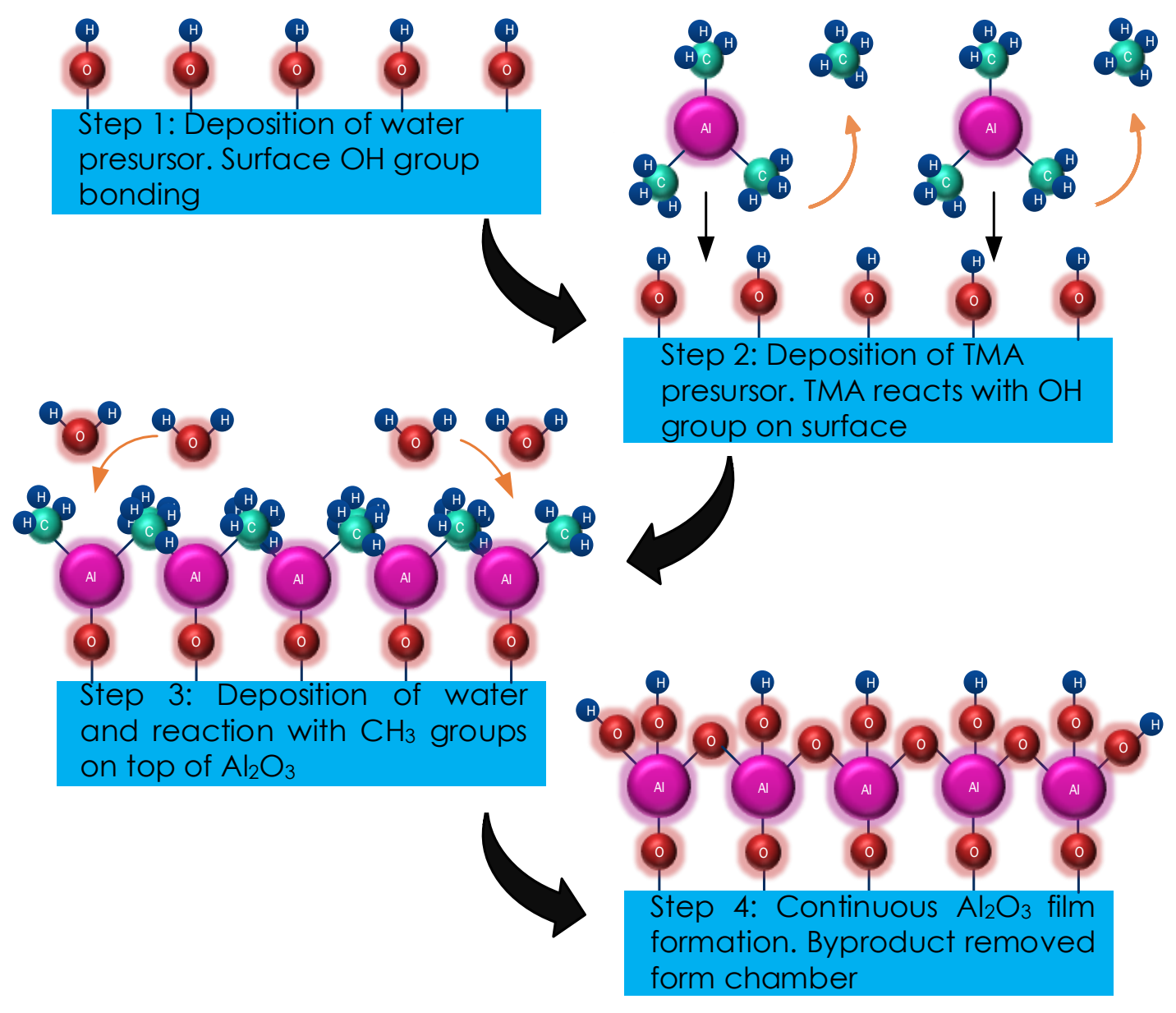


Fig. 3. SEM images of the black silicon nano-structure topology processed with plasma assisted mask-less RIE

Passivation Of Black Silicon With ALD Al_2O_3

ALD Al_2O_3 Passivation Process

After RIE all samples were cleaned in standard RCA cleaning solutions. Subsequently, wafers were coated with 380 cycles of ALD Al_2O_3 synthesized from trimethylaluminium (TMA) and H_2O 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 Al_2O_3 passivation procedure. The passivation layers were activated by post-deposition ALD in-situ annealing in N_2 ambient at 375-390 °C for 30 min. The resulting Al_2O_3 thickness of 37 nm was measured from polished reference samples with spectroscopic ellipsometry.


Step 1: Deposition of water presursor. Surface OH group bonding

Step 2: Deposition of TMA presursor. TMA reacts with OH group on surface

Step 3: Deposition of water and reaction with CH_3 groups on top of Al_2O_3

Step 4: Continuous Al_2O_3 film formation. Byproduct removed form chamber

Fig.4 Schematic view of ALD Al_2O_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.

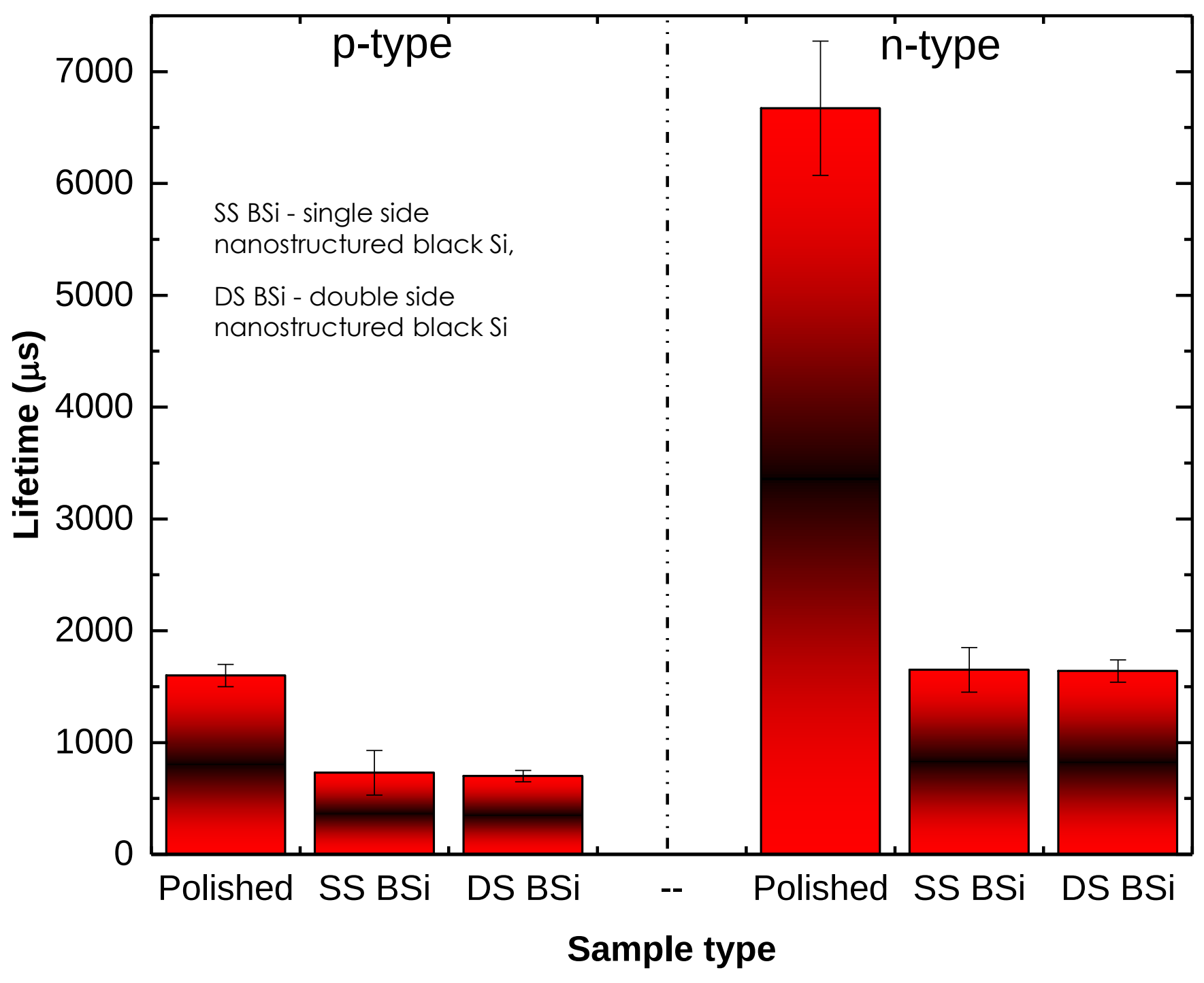


Fig. 5 Comparative graph of average lifetime wafer mapping values with standard deviation for p and n type silicon samples with polished, single side nano-structured and double side nano-structured black silicon, passivated with ALD Al_2O_3 35 nm film

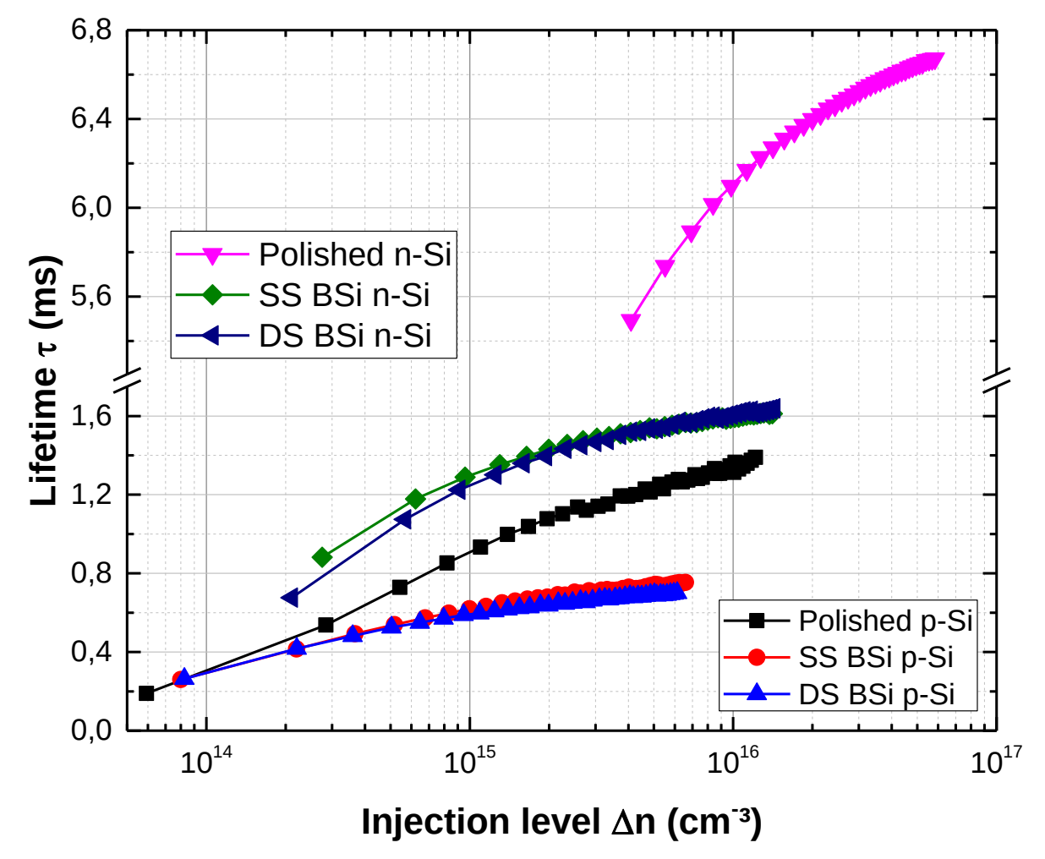


Fig. 6 Effective carrier lifetime vs. injection level

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.

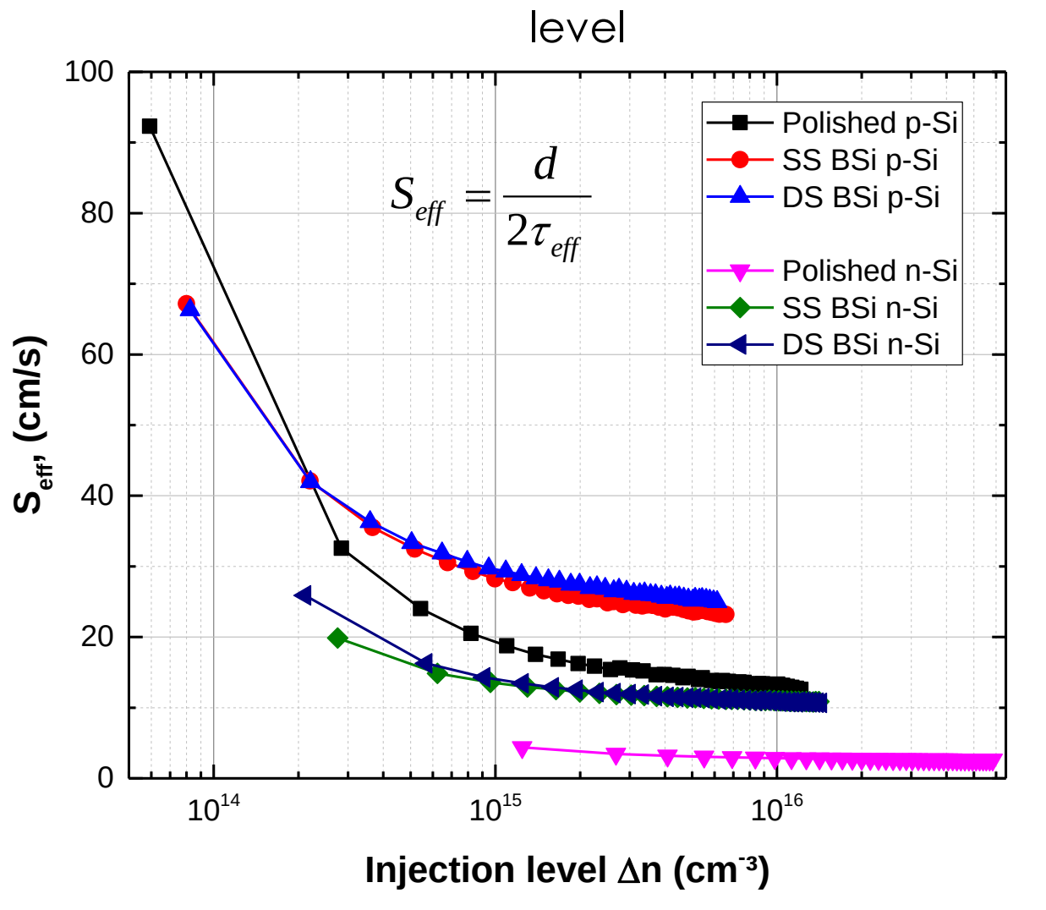


Fig. 7 Surface recombination velocity vs. injection level

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

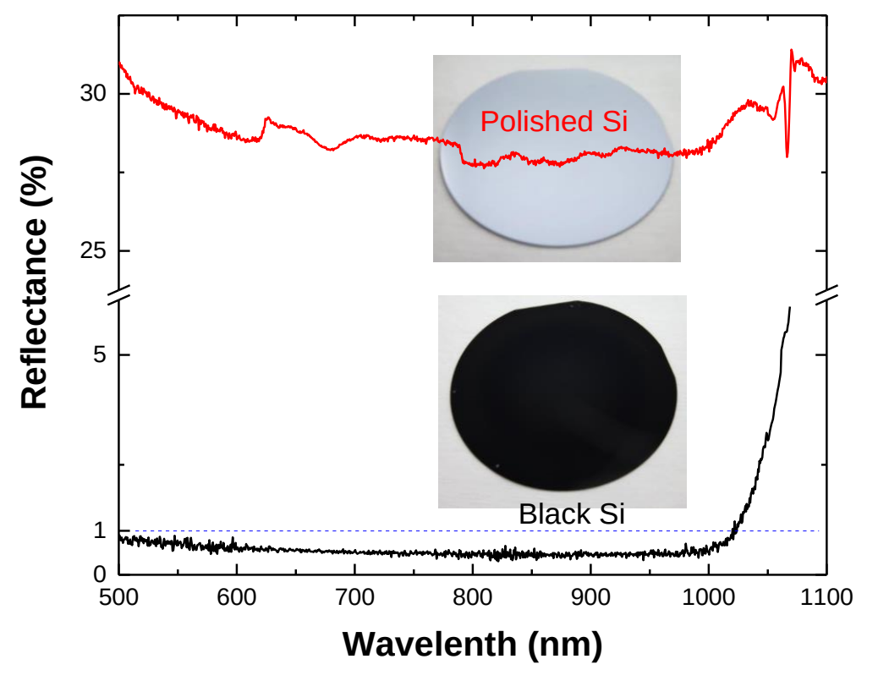


Fig. 8 Experimental reflectance spectra of polished and black silicon without Al_2O_3 coating

Future Work

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

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