BLACK SILICON FOR PHOTOVOLTAIC CELLS: TOWARDS A HIGH-EFFICIENCY SILICON SOLAR CELL

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ABSTRACT: Laser-created Black Silicon has been developed since 1998 at Harvard University. The unique optical and semiconducting properties of black silicon first led to interesting applications for sensors (photodetectors, thermal imaging cameras, etc.) Other applications like photovoltaic solar cells have been rapidly identified, but it took more than ten years of research and development before demonstrating a real improvement of the photovoltaic efficiency on an industrial multi-crystalline solar cell. This paper is a short review on recent research on the use of black silicon for photovoltaic cells.

Keywords: black silicon, hyperdoping, laser texturing, intermediate band.

The incorporation of intermediate bands, or levels, within the band gap of silicon could drastically improve the efficiency of silicon solar cells, with efficiencies well above the Shockley–Queisser fundamental limits [1-2]. Laser texturing can enhance optical density through excellent light trapping as shown in Figure 1 [3].

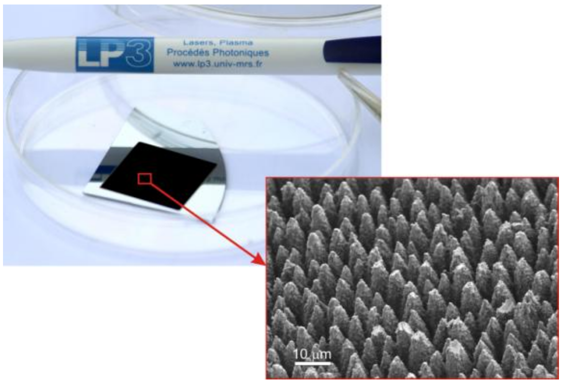

Figure 1: Visual aspect of a fs laser black silicon (fs laser, 6 kJ/m^2, 100 shots/area under SF$_6$ gas).

This texturing can be performed using nanosecond (ns), picosecond (ps), and femtosecond (fs) lasers.

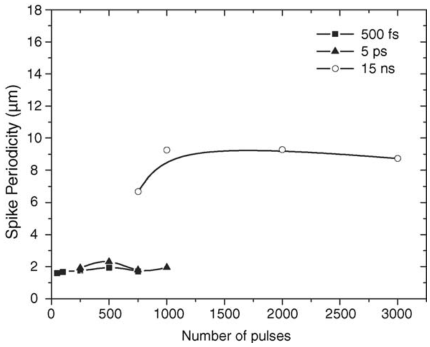

Figure 2: Structure periodicity for different KrF laser pulse durations (450 fs, 5 ps, 15 ns) as a function of number of pulses (from E. Skantzakis et al, Ref [5]).

When using ns lasers, however, the interaction mechanisms lead to much bigger microstructures (Fig. 2) and a higher thermal budget than when using ps and fs pulses [4-7].

Using short-pulse laser irradiation in the presence of a precursor gas can introduce deep donor states (or bands, depending on doping level) into the host material, with concentrations above the maximum solid solubility limit [8-17]. This hyperdoped silicon shows strong visible and sub-gap absorption (Fig. 3) that makes it a candidate for novel photodetectors and for semiconductor-based solar energy harvesters [18-37], with the potential for both low cost and high photoconversion efficiency.

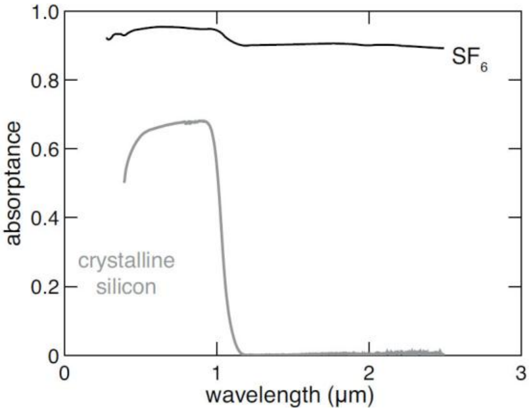

Figure 3: Absorptance of black silicon (SF$_6$) and crystalline silicon. Heavy chalcogen dopant (like S, Se, and Te) lead to remarkable optical properties including strong absorption at photon energies well below the band gap of silicon.

Control of the texturing and doping processes and development of potential applications require a good knowledge of black silicon's formation mechanisms. Therefore, numerical simulations have been used in the past few years to understand the mechanisms of formation of the initial surface structures (laser-induced periodic surface structures, or LIPSS) and how they evolve into the spike structures that characterize black silicon (Fig. 4) [38-48]. Doping profiles have been studied by secondary ion mass spectrometry (SIMS) in silicon hyperdoped with SF6 using both laser doping and plasma immersion ion implantation followed by thermal annealing (Fig. 5).

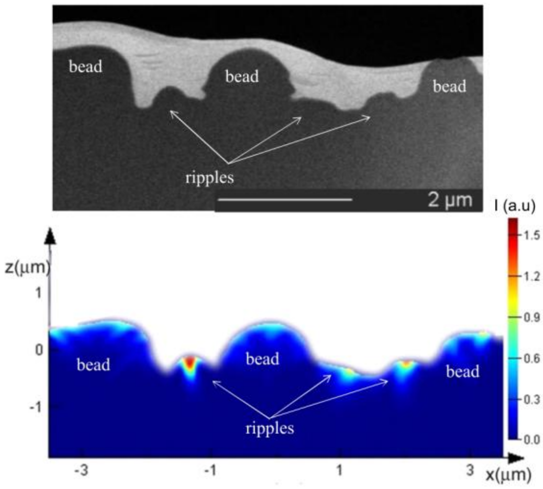

Figure 4: top: SEM cross section of a textured silicon with different structures (ripples and beads) bottom: FDTD simulation of the absorbed laser intensity (arbitrary units).

Extensive Raman, SEM and cross-section TEM studies have revealed the internal structures of the textured surface and showed the formation of metastable Si polymorphic phases (from diamond cubic Si-I into amorphous Si, Si-XII, and Si-III) [49-50].

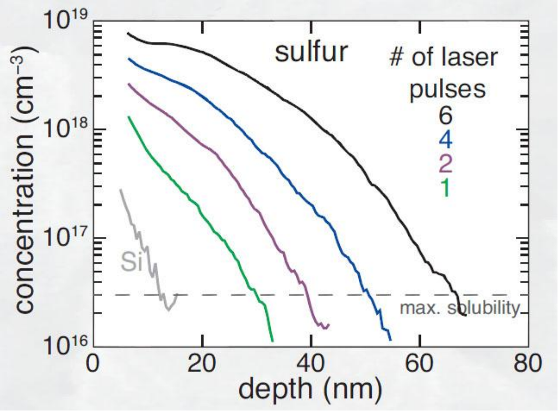

Figure 5: SIMS measurements performed after irradiation for 1, 2, 4 and 6 laser pulses. SF6 pressure is 100 Torr and the laser fluence is kept below the ablation threshold.

Amorphous Si, Si-XII, and Si-III were found to form in femtosecond-laser doped silicon regardless of the presence of a gaseous or thin-film dopant precursor (Fig. 6). The rate of pressure loading and unloading induced by femtosecond-laser irradiation kinetically limits the formation of pressure-induced phases, producing regions of amorphous Si 20 to 200 nm in size and nanocrystals of Si-XII and Si-III.

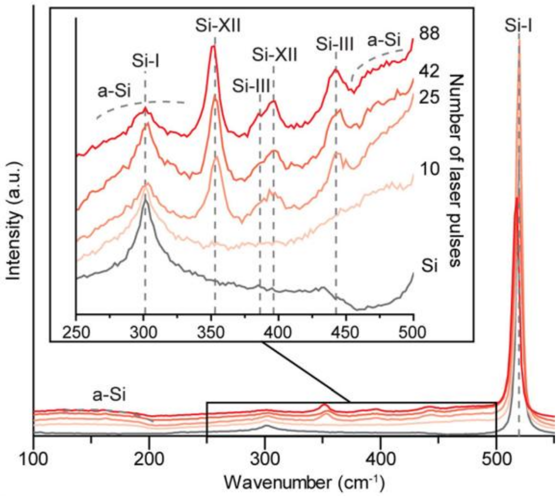

Figure 6: Stokes Raman spectra of Se:Si irradiated with an increasing number of laser pulses, offset to show the individual spectra. The inset is rescaled to highlight the Raman modes corresponding to a-Si, Si-III, and Si-XII (from M. Smith et al, Ref. [49])

These phases are usually created at very high pressures and are also known to reduce the silicon band-gap [51], even though we believe they are not directly responsible for the extended IR absorption of the black silicon.

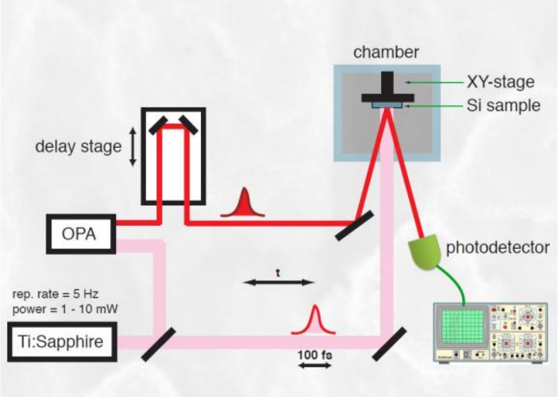

Figure 7: fs laser pump-probe set-up.

In-situ pump-probe measurements have also been performed to better understand the dynamics of the doping process (Fig. 7). Current observations suggest that fs-laser irradiation achieves hyperdoping through a process called solute trapping. fs-laser pulses with energy greater than the melting threshold transform the surface into a molten layer, enabling dopant precursors in the vicinity to diffuse in. As the deposited energy diffuses into the substrate, the molten layer resolidifies with a speed faster than the rate at which thermodynamic equilibrium can be established (>1m/s), thus trapping the dopants in their hyper-concentrated state. In order to model the doping process, experimentally probing the position of the liquid/solid interface as a function of time, i.e., the melt dynamics, is essential. Preliminary results from pump-probe set-up (Fig. x) show that the surface of the silicon transforms into a high reflectance phase in 1ps when the fluence is above 1.5kJ/m^2 and melt duration at

fluences below the ablation threshold is on the order of ns.
This ultra-fast melt dynamics is still under investigation, it will enable to model and design the dopant profile but also to give a better understanding of the ultrafast phase transformation induced by fs-laser irradiation.

Other authors [54] have also reported recently that flexible black silicon can be easily realized by texturing commercial SOI wafers and etching out its middle layer in HF (Fig. 8). They have used this thin-film black silicon mainly for solar thermal panels, thanks to its good light-absorbing and heat-transferring properties. The extreme flexibility of this black silicon film could also be interesting for high-efficiency thin-film photovoltaics.

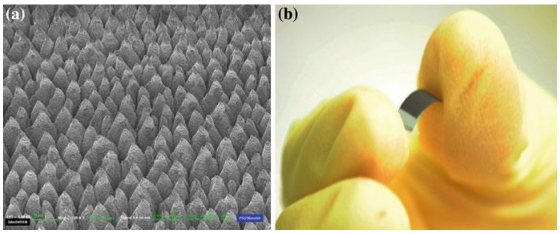

Figure 8: (a) SEM image of the flexible black silicon and (b) an illustration of the bent flexible black silicon by slight finger pressing (from W. Wei et al, Ref [54]).

In order to enhance the processing speed for photovoltaic applications, several studies have now been carried out [53, 55] to scale up the laser treatment process by means of parallelization and the use of diffractive optical elements (DOE), as shown in Figure 9.

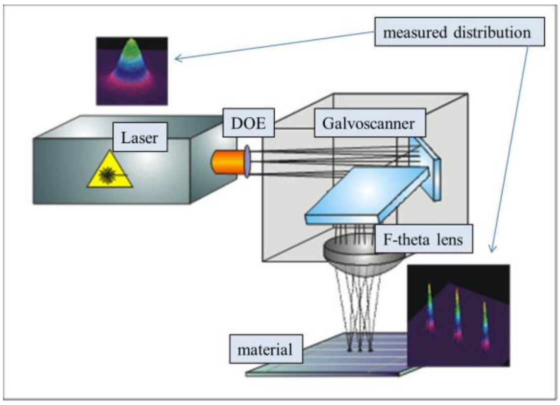

Figure 9: schematic of beam splitting by a DOE in front of the galvo-scanner (from V. Schütz et al, Ref [55]).

Black silicon solar cell photovoltaic efficiency has now increased from 2% (in 2000) up to 17% [52-53] (Sionyx, mc-Si, without hyperdoping), but the real potential has still to be demonstrated. The best solar cells using hyperdoped black silicon still have an efficiency below 10%. Realizing the potential of hyperdoped photovoltaics still requires a better understanding of the structure formation and an improvement of the carrier life time.

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