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Tailoring the absorption properties of Black Silicon

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Abstract

Samples of crystalline silicon for use as solar cell material are structured and hyperdoped with sulfur by irradiation with femtosecond laser pulses under a sulfur hexafluoride atmosphere. The sulfur creates energy levels in the silicon band gap, allowing light absorption in the infrared wavelength regime, which offers the potential of a significant efficiency increase. This Black Silicon is a potential candidate for impurity or intermediate band photovoltaics. In this paper we determine the laser processed sulfur energy levels by deep-level transient spectroscopy (DLTS). We present how the number of laser pulses per sample spot influence the sulfur energy levels and hence the DLTS spectra. Further we show that changing the laser pulse by splitting it with a Michelson interferometer setup results in altered absorption which is most likely due to altered sulfur energy levels. This contribution focuses on the possibility of controlling the sulfur in Black Silicon through manipulating the laser pulse shape. As a first step samples of microstructured silicon are fabricated with doubled laser pulses at two different laser pulse distances and the absorption spectra by integrating sphere measurements are compared.

Keywords: Black Silicon; femtosecond laser; pulse shaping; sulfur doping; infrared absorption; deep-level transient spectroscopy

1. Introduction

The capability of Black Silicon, microstructured and sulfur-doped silicon with femtosecond laser pulses, for photovoltaics has been shown [1]. The near infrared absorption of Black Silicon is enhanced through the incorporation of sulfur in the top layer with a very high concentration of sulfur donor states in

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the band gap [2]. Many of these defects are supposed to be at least extended, but more likely, due to their exceptionally high concentration, are forming an impurity band in the silicon band gap [3], resulting in an increase of infrared absorption over a wide wavelength range [4]. The infrared absorption depends on the sulfur content in the sample after laser irradiation [5] and on the temperature during a post-laser process annealing step [6]. The sulfur content as well as the way the sulfur is incorporated in the silicon are important when considering this material for photovoltaic applications. In this paper deep-level transient spectroscopy (DLTS) measurements [7] are conducted on microstructured silicon. Samples processed with doubled laser pulses at two different double pulse distances show different absorption values in the near-infrared wavelength regime.

The samples used are Boron-doped Czochralski and Float Zone silicon wafer pieces of 1 cm^2 and 4 cm^2 with a thickness of 525 µm and 380 µm, crystal orientation (100) and specific resistance of 0.3 – 0.38 and 1 – 5 Ωcm. A titan-sapphire-laser with a central wavelength of 800 nm is used to process the samples in a vacuum chamber under sulfur hexafluoride atmosphere. The scanning velocity determines the number of femtosecond laser pulses N per sample spot.

In this paper three different laser pulse numbers are investigated: $N = 1$, $N = 5$ and $N = 500$. The surfaces respectively show a pink, grey and a black finish to the naked eye due to the higher light absorption as consequence of bigger microstructures on silicon treated with an increasing number of pulses per spot. These three different types of microstructured silicon are therefore called Pink, Grey and Black Silicon.

Nomenclature

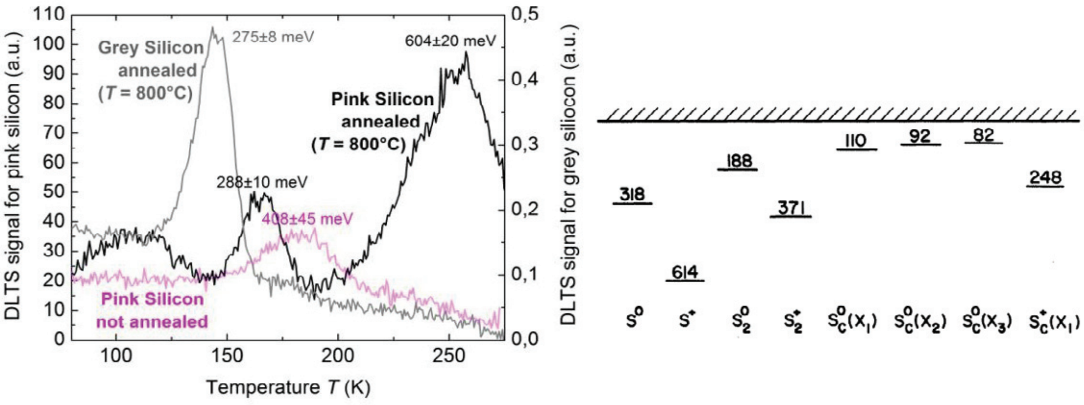
N	Number of femtosecond laser pulses per sample spot
ΔE	Energy difference of band edge and deep-level
Δt	Double pulse distance

2. Experimental

2.1. Deep-Level Transient Spectroscopy Measurements

First DLTS measurements on laser microstructured silicon are performed on samples of Pink Silicon and Grey Silicon. The measurements on Pink Silicon are made on solely laser processed samples as well as on samples, additionally annealed at 800 °C for 30 minutes. The results are shown in Fig. 1(a). Possible sulfur energy states in the silicon band gap are shown in Fig. 1(b).

Before annealing Pink Silicon, the DLTS spectrum is dominated by a defect signal referring to an activation energy around $\Delta E = 408$ meV, which may correspond to the S_2^+ sulfur state. After annealing this level changes to $\Delta E = 288$ meV, possibly corresponding to the S^0 or $S_C^+(X_1)$ defect, and $\Delta E = 604$ meV, which lies around the energy of the S^+ sulfur defect. With respect to the broadening of the peak at 604 meV, it is most likely an extended defect rather than a point defect. A deeper insight is expected from further investigations. Annealed Grey Silicon exhibits one energy level at $\Delta E = 275$ meV which is most likely either the S^0 or the $S_C^+(X_1)$ sulfur defect. This indicates that sulfur states are present in the band gap of microstructured silicon and that they change with the annealing step after laser processing.



(a) (b)

Fig. 1. (a) DLTS spectra for annealed, not annealed Pink Silicon (1 pulse per spot), and annealed Grey Silicon (5 pulses per spot); (b) Sulfur energy levels in the band gap of silicon [8]

Absorption spectra of samples processed with the same parameters as those used for the DLTS measurements are shown in Fig. 2. Absorption differences in the visible range being due to the different surface morphologies, the difference in the infrared range is caused by the sulfur and may partly be owing to the different sulfur energy levels present in the material.

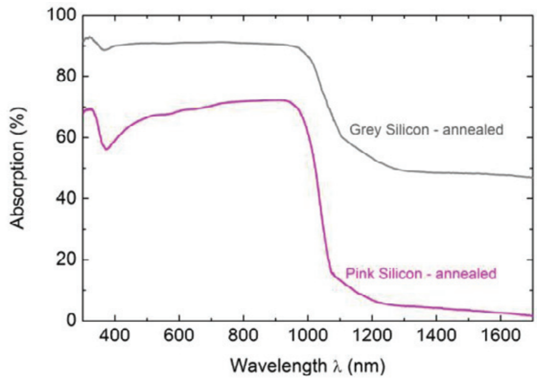


Fig. 2. Absorption spectra of annealed Pink and Grey Silicon, obtained through integrating sphere measurements

Since the absorption as well as the solar cell suitability of Black Silicon depends on the sulfur, our idea is to influence the sulfur in a way other than annealing. By using a different pulse form during the laser process itself, the process may be shortened by the annealing step.

2.2. Silicon microstructured with doubled laser pulses

Grey Silicon samples ($N = 5$) as well as Black Silicon samples ($N = 500$) are processed with laser pulses doubled through a simple Michelson interferometer setup. Two different double pulse distances Δt are used, $\Delta t = 50$ fs and $\Delta t = 100$ fs, and are examined, concerning the infrared absorption.

The absorption in the visible and near-infrared range is shown in Fig. 3. The overall absorption was found to be similar for samples processed with 500 pulses per sample spot. Here the number of pulses

(500) dominates over the influence of the double pulses spacing.

For samples processed with 5 pulses per spot the absorption in the visible range is for both pulse distances only slightly different. In the infrared range, samples at a pulse distance of 100 fs show a higher absorption.

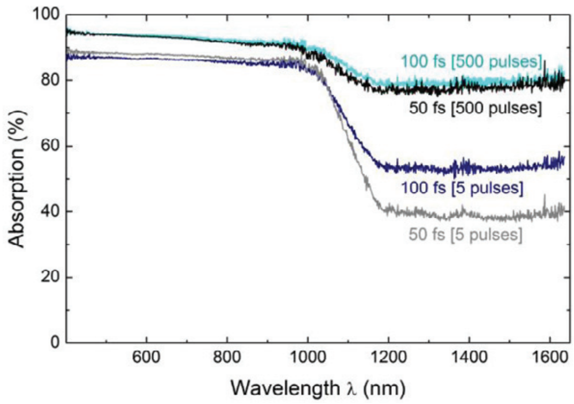


Fig. 3. Absorption in the visible and infrared range of Grey and Black Silicon samples fabricated at double pulse distances Δt = 50 fs and 100 fs

3. Discussion

Any differences in absorption for Grey Silicon, made at different double pulse distances, can be caused by two factors only: first the sulfur that is incorporated in the surface could be responsible – either there is more (or less) sulfur or it is incorporated in a different way; second the cristallinity of the surface could be a valid factor for the visible range. In the infrared range, however, the most probable assumption as a reason for the absorption difference is the sulfur content in the surface layer, as the sulfur plays a leading role in the extent of the infrared absorption of femtosecond laser structured silicon.

Further investigations are necessary to determine the exact source of the absorption differences as well as additional DLTS measurements to obtain a more complete picture of the dependence of sulfur states and thus of the absorption on the pulse shape.

On the one hand the sulfur energy states enhance infrared absorption, on the other hand they might increase Shockley-Read-Hall (SRH) recombination [9,10]. As this work indicates that laser pulse shaping may be a method to manipulate sulfur energy levels, there is the chance that shaped laser pulses are also capable of tailoring the high impurity concentration levels and thereby the impurity band placement and width in order to decrease or suppress SRH recombination as indicated by [11].

Overall Black Silicon combined with laser pulse shaping seems to be a promising route to new methods of controlling the sulfur levels and therefore the absorption of Black Silicon.

Acknowledgements

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