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Light-induced reflectivity transients in black-Si nanoneedles

P. Ščajev [a,*], T. Malinauskas [a], G. Seniutinas [b,c], M.D. Arnold [d], A. Gentle [d], I. Aharonovich [d], G. Gervinskas [b,c], P. Michaux [b], J.S. Hartley [b], E.L.H. Mayes [e], P.R. Stoddart [b], S. Juodkazis [b,c]

[a] Institute of Applied Research, Vilnius University, Saulėtekio Avenue 9, Bldg. III, LT-10222 Vilnius, Lithuania
[b] Faculty of Science, Engineering and Technology, Swinburne University of Technology, Hawthorn VIC 3122, Australia
[c] Melbourne Centre for Nanofabrication, ANFF, 151 Wellington Road, Clayton VIC 3168, Australia
[d] School of Mathematical and Physical Sciences, University of Technology Sydney, 15 Broadway, Ultimo NSW 2007, Australia
[e] School of Applied Sciences, RMIT University, GPO Box 2476 V, Melbourne VIC 3001, Australia

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ABSTRACT

The change in reflectivity of black-Si (b-Si) upon optical excitation was measured by the pump-probe technique using picosecond laser pulses at 532 (pump) and 1064 nm (probe) wavelengths. The specular reflection from the random pattern of plasma-etched b-Si nano-needles was dominated by the photo-excited free-carrier contribution to the reflectivity. The kinetics of the reflectivity were found to be consistent with surface structural and chemical analysis, performed by scanning and transmission electron microscopy, and spectroscopic ellipsometry. The surface recombination velocity on the b-Si needles was estimated to be $\sim 10^2$ cm/s. Metalization of b-Si led to much faster recombination and alteration of reflectivity. The reflectivity spectra of random b-Si surfaces with different needle lengths was modeled by a multi-step refractive index profile in the Drude formalism. The dip in the reflectivity spectra and the sign reversal in the differential reflectivity signal at certain b-Si needle sizes is explained by the model.

1. Introduction

The fabrication and replication of nano-textured surfaces is a fast growing area of research, especially in the biomedical field where surface structures can have a significant effect on the functions of cells and membrane receptors [1]. When coated with thin films or nanoparticles of plasmonic metals, nanostructured surfaces are also widely employed as substrates for surface-enhanced Raman scattering (SERS) [2,3]. In this context, black-Si (b-Si) has attracted increasing attention, as the surface area, aspect ratio of the nano-needles, surface hydrophobicity, changes in the surface recombination rate and antireflection properties are all very useful parameters for energy and sensing applications [2,4,5].

The surface structure and properties of b-Si can be controlled via the plasma- or chemical- etching conditions used in fabrication. Black-Si solar cells with high efficiency ($>18\%$) have been achieved [6], even without an antireflection coating. The tapered needles create a gradual change in refractive index, which reduces the reflectivity of a step-like change in refractive index, as demonstrated in the case of glass [7] and in some naturally nanostructured surfaces [8]. The porosity of Si can also be controlled by electrochemical etching to change the refractive index and surface passivation [9]. Future solar cells with light harvesting efficiencies of over 90% and a Si thickness of just micrometers have been designed using slanted conical holes [10].

In all of these light harvesting and sensor applications, structural defects and chemical contamination on the surface of plasma- (or chemically-) etched surfaces have to be understood and controlled. This study explores the effect of plasma etching on light localization, absorption and thermal properties, using a picosecond pump-probe spectroscopy technique to investigate the photoinduced reflectivity of b-Si. Black-Si with different morphologies was prepared by plasma etching. The unperturbed reflectivity of random b-Si surfaces was modeled by a multi-step refractive index profile and matched to experimental ellipsometry data.

2. Results

All of the samples in this study were made by the same plasma etching recipe, but with different etching times. Fig. 1 shows SEM images of b-Si etched for 5 min ((a), (b)) and 25 min ((c), (d)). The separation between the b-Si needles followed a diffusional dependence on etching time, with an average separation of

* Corresponding author.
E-mail addresses: Patrik.Scajev@ff.vu.lt (P. Ščajev), SJuodkazis@swin.edu.au (S. Juodkazis).

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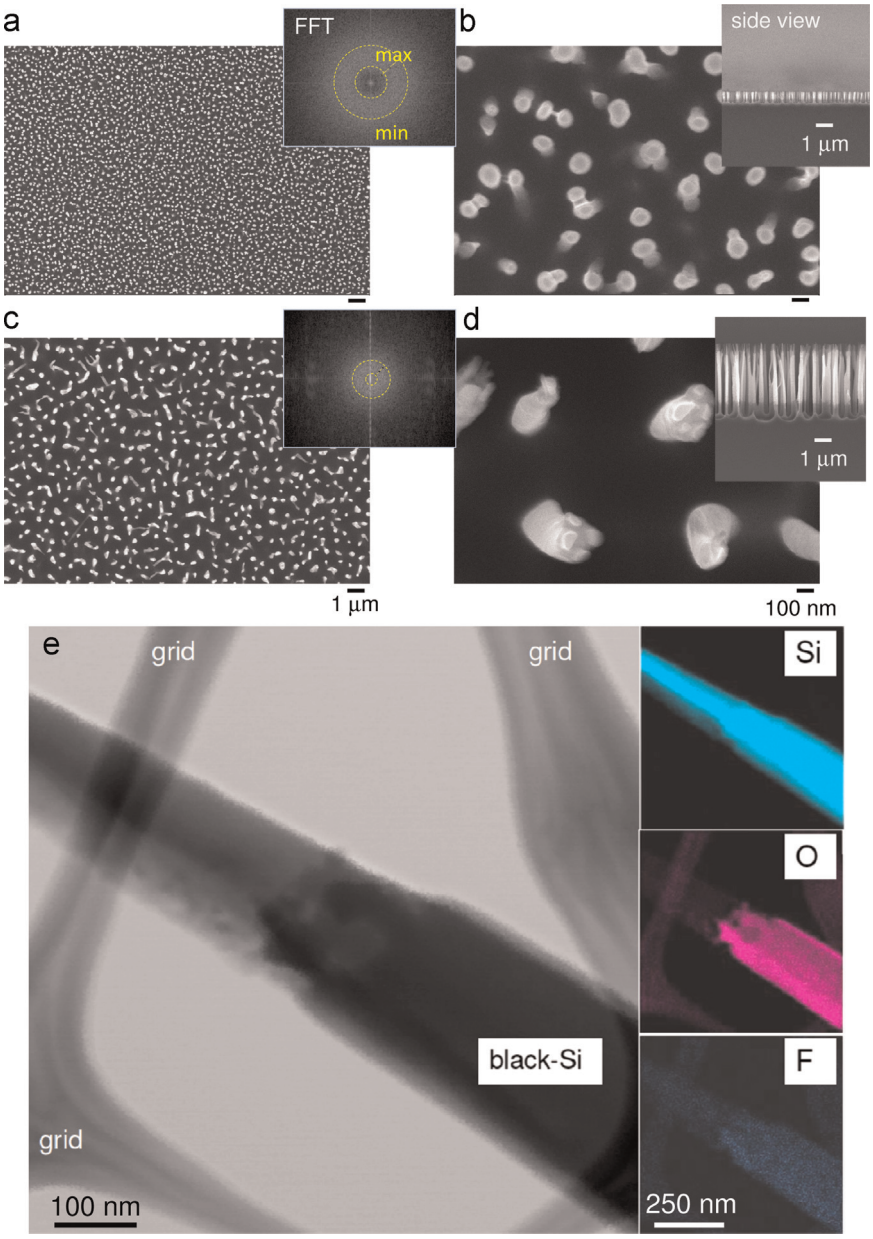

Fig. 1. Top view SEM images of b-Si etched for 5 min (a), (b) and 25 min (c), (d) (Batches 2 and 3, respectively). Insets in (a), (c) are fast Fourier transform (FFT) images with the inner (max) and outer (min) dashed-circles corresponding to 692–261 nm (max–min) in (a) and 1635–573 nm in (c). Insets in (b), (d) are side-view SEM images. (e) Elemental mapping was conducted using scanning-TEM mode and an EDS detector (Batch 3).

388 ± 20 nm for 5 min and 842 ± 30 nm for 25 min etch times (Fig. 1). For Batch 1, the separation was $\sim$ 300 nm and the pillars had a pyramidal shape of height $\sim$ 500 nm. Batches 1–2 had comparable pillar heights [12], while Batch 3 has a pillar height of 4 μm as evident from Fig. 1(d).

Fig. 1(e) shows the surface chemical composition and morphology of a sample from Batch 3. X-ray photo-electron spectroscopy (XPS) revealed no significant differences between samples from Batches 1–3. Surface contamination by fluorine and oxygen was present due to the mixture of SF_6 and O_2 used for plasma etching. The tips of the needles were crystalline silicon without any amorphization or distinct oxide layer. This is an important point, as it allowed the optical response to be modeled without having to account for changes in surface composition.

The reflectivity of the samples was measured with a bifurcated optical fiber spectrometer, where white light illumination was delivered via the central fiber and the back-reflected (and scattered) light was collected by satellite fibers. As shown in Fig. 2, a recognizable reflectivity dip was observed and its spectral position and amplitude were dependent on the structure of the b-Si.

Although the reflection from the b-Si was low ($\sim$ 1–2%), it was close to specular. In a pump-probe experiment, specular reflection is not expected when the wavelength of the pump laser is smaller than the spacing between the needles. However, the reflectivity measured by pump-probe at a distance tens-of-centimeters from the b-Si surface was comparable to that measured with the bifurcated fiber spectrometer directly at the surface. Hence, reflectivity (transmission) measurements can be carried out under laser illumination, providing a contactless optical measurement of excited carrier dynamics in the sub-surface regions of the needles.

The differential reflectivity, $DR(t)$, is defined in terms of the time-dependent sample reflectivity $R(t)$ and the equilibrium reflectivity R_0 (see Eq. (1)) [11]. The differential reflectivity kinetics