Silicon nanowires by self-organised reactive ion etching

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Abstract

Dense arrays of vertically-aligned nanowires were fabricated using a self-masking SF_6/O_2 dry etch process. Oxygen flow rate and etch time were varied and an argon plasma etch was employed to taper the resulting nanowire features. The surfaces exhibit very low reflectivities across a range of wavelengths and angles of incidence. Weighted average reflectances as low as 0.05% are demonstrated, showing high potential for PV applications.

Introduction

Nanowires, formed by bottom-up vapour-liquid-solid (VLS) techniques or by top-down etching techniques can create antireflective (AR) structures by assisting multiple reflections between or within wires, or by inducing gradual changes of refractive index like moth-eye AR schemes [1]. Nanowires can also enhance absorption and modify bandgaps as a result of quantum confinement if dimensions are small enough. Within PV, nanowires can form nanoscale core-shell solar cells, can be used as AR or enhanced absorption surfaces and can be used as a textured substrate [2–4],

In our research we are primarily interested in the AR properties of nanowires and their use as a textured substrate for thin film silicon solar cells. In this paper we describe the fabrication and characterisation of self-organised "silicon-grass" nanowires formed by reactive ion etching (RIE) in a process similar to that reported by Pezoldt *et al.* [5], which is based on the "Black Silicon Method" by Jansen *et al* [6]. The nanoscale features form without the need for a lithographically defined mask and so the process is relatively cheap and scalable compared to other nanoscale texturing technologies. We describe the conditions for optimized nanowire formation and present reflection spectra at normal incidence, from which we extract an average reflectance, weighted to the AM 1.5 solar spectrum, as a figure of merit for AR performance under sunlight. Finally, we show the reflectance spectrum over a range of incident angles a sample treated to an argon plasma etch designed to taper the nanowires and so further enhance the AR performance of the array.

Method

Sample Fabrication

A 2 cm × 2 cm section of a p-type silicon wafer was used as the starting material for the formation of the nanowire texture. Following an RCA clean, the sample was loaded into the reactor chamber (STS LPX Pegasus de-coupled ASE ICP DRIE), details of which are described in [5]. Mixed mode etching (etching and simultaneous passivation) proceeds with an SF_6/O_2 plasma whereby the etch time and the oxygen flow rate can be varied to control the resulting surface texture. Process parameters are shown in Table 1.

SF_6 gas flow	60 sccm
O_2 gas flow	85,95,105 sccm
Platen Power	50 W
Chamber pressure	15 mTorr
Chamber temperature	20 C˚
Process time	20,30,60 sec

Table 1: Process parameters for fabrication of "silicon-grass" nanowires.

Additional Ar plasma etching was applied to some samples to further shape the nanowire features.

Sample Characterization

Samples were cleaved to allow cross-sectional scanning electron microscopy (SEM) to be carried out. SEM was performed with a Carl Zeiss NVision40 FIB equipped with a Gemini FEGSEM column. The beam energy was 20 keV. The samples were mounted vertically in the SEM and tilted by 10° so that the images were captured at 80° from the normal to the surface. The height of the nanowire features was obtained as an average of several measurements taken directly from the cross-sectional SEM images, accounting for the sample tilt.

A reflectance probe technique was used to measure the reflectance spectra from the nanowire samples (Figure 1). The probe (Ocean Optics) delivers light from a white light source (HL-2000 tungsten-halogen, Ocean Optics) to the sample through six optical fibres. A central optical fibre collects a proportion of light reflected from the sample and delivers this to a spectrometer (USB4000, Ocean Optics). Bare silicon was used as a reflectance standard and the theoretical reflectance spectrum for this was used to produce graphs of absolute reflectance (R_{samp}) vs. wavelength (λ) (Equation 1).

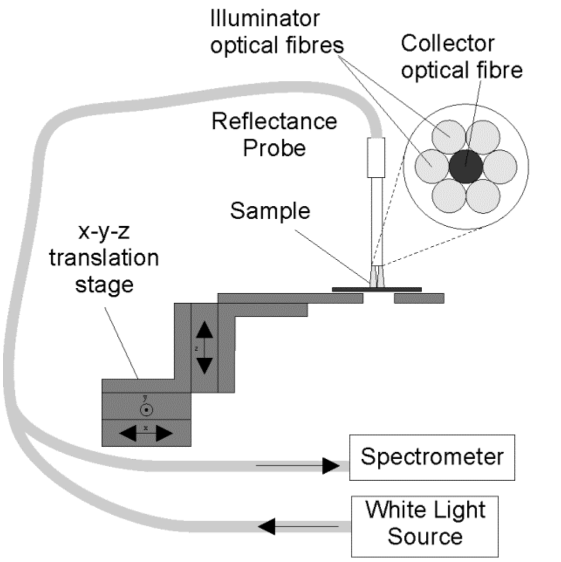

Figure 1. Reflectance probe measurement set-up.

$$R_{samp} = \frac{I_{samp}(\lambda) - D(\lambda)}{I_{stan}(\lambda) - D(\lambda)} \times R_{stan}(\lambda) \quad (1)$$

Here, I_{stan} and I_{stan} are the reflected intensities from the sample and standard, respectively, D is the dark intensity and R_{stan} is the theoretical reflectance of the standard (polished Si).

The weighted reflectance (R_w) was calculated using equation 2, where PFD is the AM 1.5 solar spectrum in the form of photon flux density, in units of photons/m^2/s.

$$R_W = \frac{\sum\left[R_{samp}(\lambda) \times PFD(\lambda)\right]}{\sum\left(PFD(\lambda)\right)} \quad (2)$$

Specular reflectance spectra (470 nm – 800 nm) over a range of incident angles (12°-80°) was measured using a θ-2θ reflectometer. Broadband light (supercontinum laser, Fianium) was directed at the sample and a detector fibre, connected to a spectrometer and mounted on an arm with a centre of rotation at the sample was positioned to collect the specularly reflected beam. The sample angle was rotated to vary the incident angle and the collector arm was simultaneously rotated by twice the angle to follow the specularly reflected beam.

Results

Nanowire morphology

The plasma etching process creates a dense array of high aspect ratio, vertically aligned nanowires, (Figure 2 and Figure 3) the height and density of which can be controlled by varying the etch time and O_2 flow rate. Details of the etching and passivation mechanisms that lead to this type of surface are explained in detail elsewhere [5], [6].

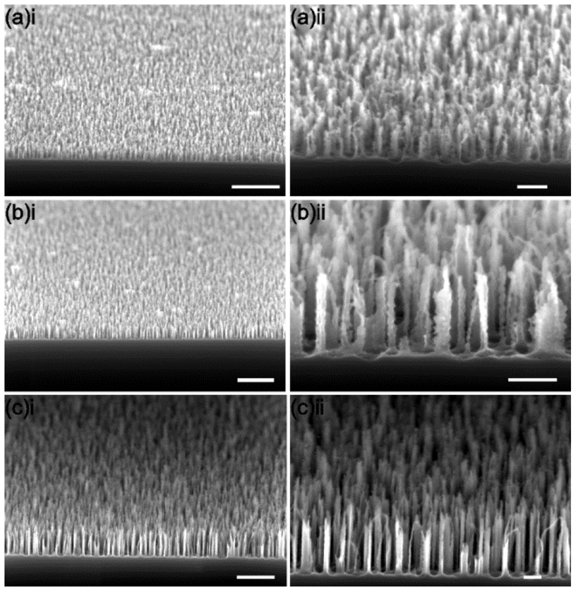

Figure 2. SEM images of textured silicon surfaces etched for the following times: (a) 20 s (b) 30 s and (c) 60 s. The oxygen flow rate was 85 sccm. The scale bars are (i) 2 µm and (ii) 400 nm.

The average height is proportional to the etching time (Figure 4). Increasing the oxygen flow rate increases the apparent density of the nanowires as seen using SEM (Figure 3), whilst decreasing the average height (Figure 4). It is clear from the plot in Figure 4 that the range of times tested had a larger effect on the average height than the range of O_2 flow rates tested.

Surface reflectance

Spectral reflectance measurements demonstrate that all samples have an AR effect, with the reflectance decreasing with increased etch time (Figure 5) and oxygen flow rate (Figure 6).

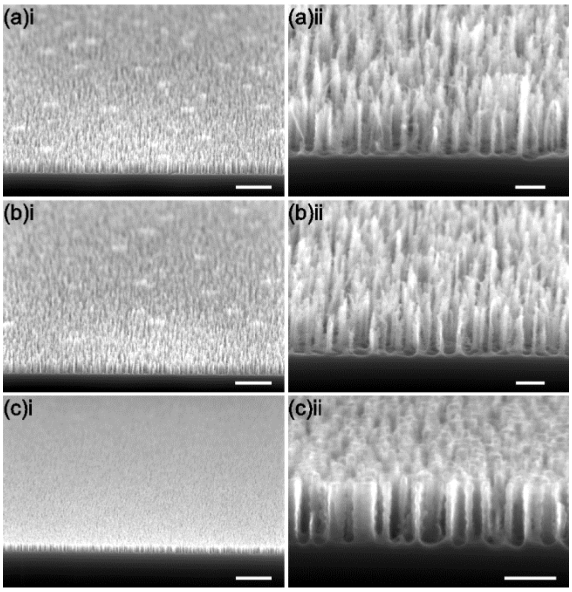

Figure 3. SEM images of textured silicon surfaces etched for 30 s, using an oxygen flow rate of (a) 80 sccm, (b) 95 sccm and (c) 105 sccm. The scale bars are (i) 2 μm and (ii) 400 nm.

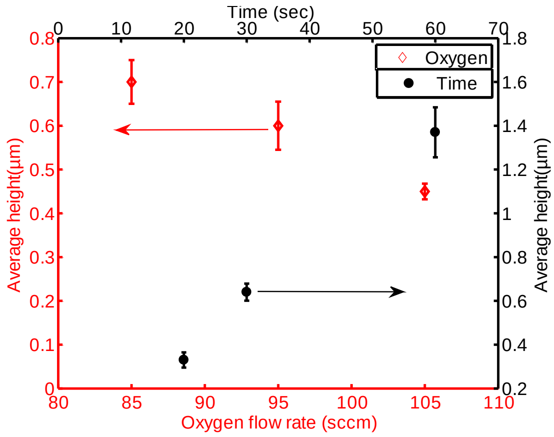

Figure 4. Plot of average nanowire height vs. oxygen flow rate and etch time.

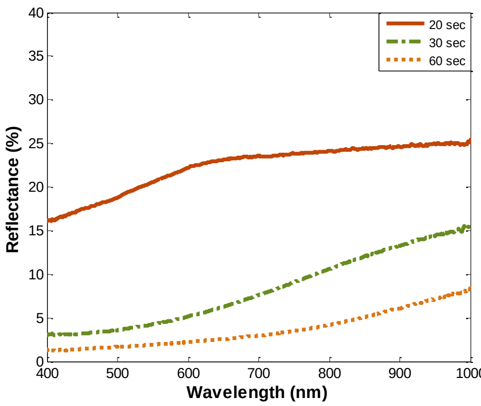

Figure 5. Reflectance probe measurement results showing the reflectance spectra for textured silicon surfaces etched with an oxygen flow rate of 85 sccm for various times.

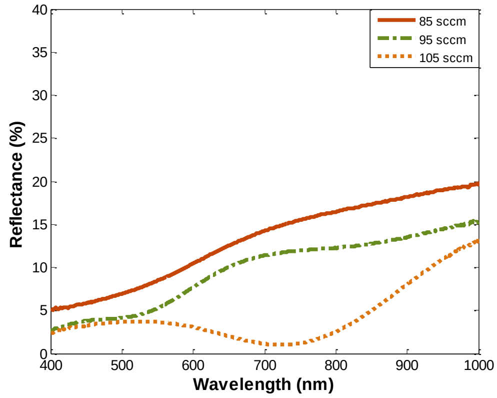

Figure 6. Reflectance probe measurement results showing the reflectance spectra for textured silicon surfaces etched for 30 s, and various oxygen flow rates.

To quantify this behaviour in terms of the texture's PV applicability, the average reflectance weighted to the AM1.5 solar spectrum (R_w) was calculated and plotted as a function of etch time and oxygen flow rate (Figure 7). As the etch time is increased, the nanowire feature height increases, reducing reflectance by increasing the region over which the effective refractive index is graded. The same trend is not seen with O_2 flow rate where the height is seen to decrease but the reflectance also decreases. Here, the improved AR effect due to the increase in feature density appears to more than compensate for the decrease in height.

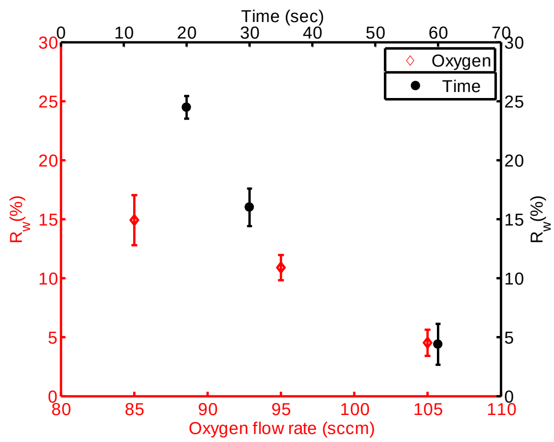

Figure 7. Average reflectance, weighted to the AM1.5 solar spectrum, as a function of etch time and oxygen flow rate.

Argon treatment

A 3 minute Ar plasma treatment can be used to modify the appearance of the nanowire features as seen in the before (a) and after (b) SEM images in Figure 8. The Ar treatment decreases the side wall slope of the nanowires, resulting in tapered features. From an effective medium viewpoint, this step alters the effective refractive index profile from air to silicon. The measurements of specular reflectance over a range of wavelengths and angles of incidence (Figure 9) show that the AR performance improves after argon treatment as the tapering creates a graded index profile that is closer to optimum. The R vs. λ and θ maps clearly demonstrate the broadband nature of the AR effect and the wide angular range over which it operates compared to bare polished silicon. The weighted average reflectivities of the surfaces shown in Figure 8 are 0.13% ±0.08 (without Ar treatment) and 0.05%±0.02 (with Ar treatment).

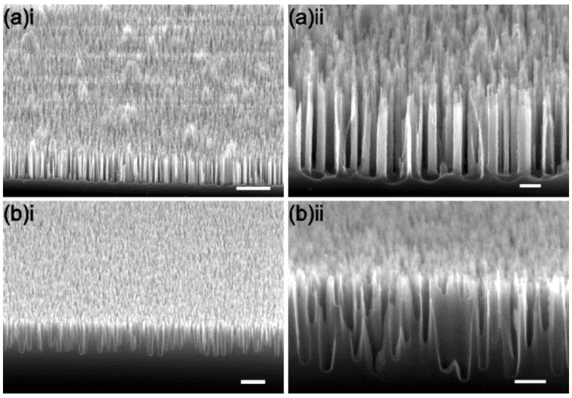

Figure 8. SEM images of textured silicon surfaces etched using an oxygen flow rate of 100 sccm for 2 mins; (a) without and (b) with a 3 minute Ar treatment. The scale bars are (i) 2 µm and (ii) 400 nm.

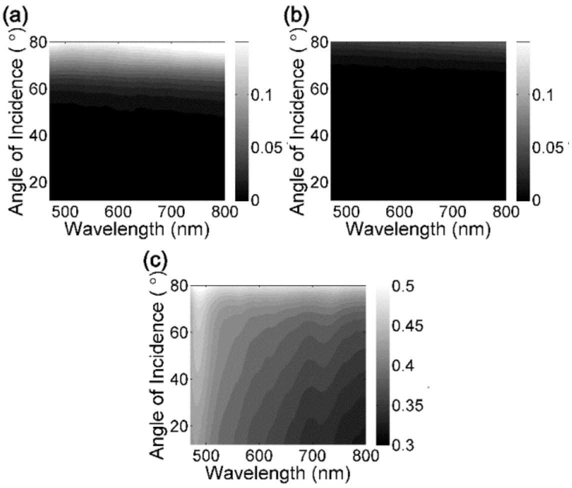

Figure 9. Measured specular reflectance as a function of wavelength and angle of incidence for the textured silicon samples shown in Figure 8, (a) without and (b) with a 3 minute Ar treatment. (c) Results from a bare polished silicon sample for comparison.

Conclusions

Highly effective nanowire-type AR surfaces were fabricated in silicon using a self-masking SF_6/O_2 dry etch process. The resulting structures were characterized by SEM, reflectance probe and angular dependent reflectometry. Reflectance decreased with both etch time and oxygen flow rate due to the morphological changes induced by varying these parameters. An argon plasma etch was employed to taper the nanowire features, resulting in a weighted average reflectance of only 0.05%.

Future work will include a full characterization of the specular and diffuse components of reflected light by wavelength and angle resolved spectroscopy (WARS).

References

[1] S. A. Boden and D. M. Bagnall, “Tunable reflection minima of nanostructured antireflective surfaces,” *Applied Physics Letters*, vol. 93, no. 13, p. 133108, 2008.

[2] B. Tian et al., “Coaxial silicon nanowires as solar cells and nanoelectronic power sources.,” *Nature*, vol. 449, no. 7164, pp. 885-9, Oct. 2007.

[3] M. D. Kelzenberg et al., “Photovoltaic measurements in single-nanowire silicon solar cells.,” *Nano letters*, vol. 8, no. 2, pp. 710-4, Feb. 2008.

[4] L. Tsakalakos, J. Balch, J. Fronheiser, B. a. Korevaar, O. Sulima, and J. Rand, “Silicon nanowire solar cells,” *Applied Physics Letters*, vol. 91, no. 23, p. 233117, 2007.

[5] J. Pezoldt, T. Kups, M. Stubenrauch, and M. Fischer, “Black luminescent silicon,” *Physica Status Solidi (C)*, vol. 8, no. 3, pp. 1021-1026, Mar. 2011.

[6] H. Jansen, M. D. Boer, R. Legtenberg, and M. Elwenspoek, “The black silicon method: a universal method for determining the parameter setting of a fluorine-based reactive ion etcher in deep silicon trench etching with profile control,” *Journal of Micromechanics and Microengineering*, vol. 5, no. 2, pp. 115-120, Jun. 1995.