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BLACK SILICON WITH SUB-PERCENT REFLECTIVITY: INFLUENCE OF THE 3D TEXTURIZATION GEOMETRY

K. N. Nguyen[1], *D. Abi-Saab*[1], *P. Basset*[1], *E. Richalot*[2], *F. Marty*[1],
D. Angelescu[1], *Y. Leprince-Wang*[3], *T. Bourouina*[1]
[1]Université Paris-Est, ESYCOM, ESIEE Paris, Noisy-le-Grand, France
[2]Université Paris-Est, ESYCOM, UMLV, Noisy-le-Grand, France
[3]Université Paris-Est, LPMDI, Noisy-le-Grand, France

ABSTRACT

In this paper we study the impact of the three-dimensional geometry of a micro/nanostructured silicon surface on its reflectivity under incident electromagnetic (EM) illumination. We simulate the optical reflectance of 3D micro/nano silicon cones of different dimensions. Based on the favorable simulation results, maskless textured silicon, called “black silicon” is processed by deep reactive ion etching (DRIE) under cryogenic temperatures. By varying the process parameters, we fabricate conical black silicon substrates with excellent anti-reflective behavior. Notable among the results, one of the samples exhibits the lowest reflectivity in the optical wavelength published to date for plasma-etched black-silicon.

KEYWORDS

Black silicon, Cryogenic DRIE, light absorbing surface

INTRODUCTION

Silicon remains the most widely used substrate material in microtechnology thanks to the availability of the processing facilities and its reduced cost. The natural reflectance of flat silicon/air interface is around 30% because of the high refractive index of silicon. Reducing the reflection of ordinary bulk silicon has become an active research domain mainly for photovoltaic applications. Surface texturing is an effective technique to reduce the reflectance because the produced oblique incidence of light on the semiconductor surface allows multiple reflections, leading to a kind of light trapping. Such textured surfaces can also be interesting because they develop large surface area.

Several techniques such as wet etching [1], femtosecond laser pulse [2], reactive ion etching [3] and deep reactive ion etching (DRIE) [4] have been previously studied for forming different profiles. Initially considered as an unwanted side-effect in DRIE processes, mask-less texturing of a polished silicon wafer can result in the formation of “grass”-like structures that appears black to the human eye, hence the name “black silicon” [3,4]. Black silicon is now recognized as an innovative material for high-efficiency photovoltaic cells [3], improved IR photodetectors [5], photonic applications [6] and superhydrophobic coatings [7]. DRIE is based on inductively-coupled plasma (ICP) of sulphur hexafluoride (SF_6) and allows anisotropic etching of silicon by taking advantage of a passivation mechanism in the sidewalls. The influence of process parameters on the black silicon structure has been actively studied [4]. However, there is no deep study concerning the impact of its 3D geometry on the reflectivity of the incident EM radiation. In this paper we demonstrate how the 3D geometry of a micro/nano-structured silicon surface impacts the EM reflectivity of a typical black silicon material. Following the simulation guidelines, we synthesize plasma-etched black silicon using a cryogenic DRIE and we performed reflectance measurement in the optical wavelengths.

FEM SIMULATIONS AND RESULTS

3D full-wave electromagnetic field simulations have been performed with HFSS^{TM} software based on the Finite Element Method. Although black silicon can be built in various shapes such as spikes, “penguin-like” structures, columns and pyramids, the simulations are performed with cones since it is one of the shapes that provides better absorption [8]. In this paper, we focus on textured surfaces formed by cones of dimensions (height and width) varying between 150 nm and 5 µm under different directions of the incident field. The objective is to study the influence of these parameters on the reflectivity of the black silicon, in order to define the best parameters that provide the lowest reflectivity of the surface.

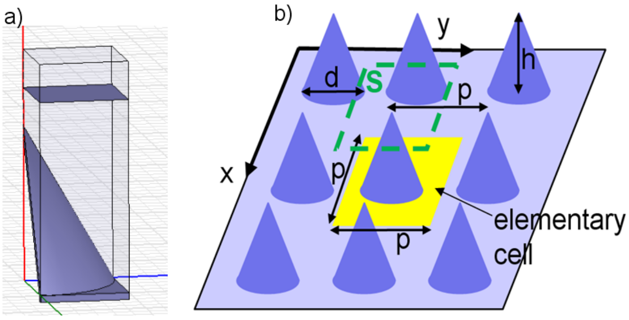

Figure 1: a) Diagram of the structure simulated by HFSS^{TM} b) 3D sketch of the simulated surface.

Description of the 3D surface

The simulated structure consists of a silicon substrate on which identical cones are periodically repeated along *x*- and *y*- axis. The structure is defined by its out-of-plane height (*h*), base diameter (*d*), and in-plane periodicity (*p*), as represented in Fig. 1. According to Floquet’s theorem [9], the structure periodicity induces the field pseudo-periodicity and allows us to reduce the computation time by restricting it to a single lattice unit with biperiodic boundary conditions [10]. The surface is excited by an incident monochromatic plane wave with a wavelength tuned from 430 nm to 1000 nm. The reflectance is obtained by calculating the ratio between the reflected and incident energies passing through a surface *S*. The surface *S* has the same dimensions as the elementary cell, and is placed above the simulated cone and parallel to the periodicity plane.

Simulation results

- Influence of the height of cones

To evaluate the influence of cone height on the reflectivity of black silicon, we have simulated a structure with identical cones with varying height. The periodicity and the width of cones are of 1.5 µm while the height is varied from 3.5 µm to 5 µm. This structure is illuminated in a direction normal to the substrate. The results shown in Fig. 2 clearly indicate that the reflectivity in the visible light spectrum decreases uniformly while increasing cone height because of multireflection of the incident light on the silicon 3D surface. We can notice that while the dependence of reflectivity on height is modest in the infrared limit (1000 nm), it is significant when observed at lower wavelengths (430-600 nm).

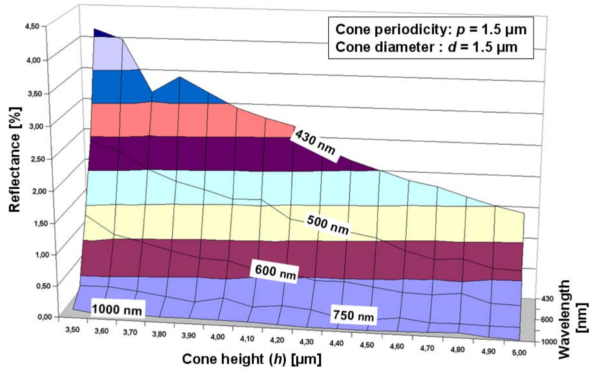

Figure 2: Cone height influence on simulated reflectivity.

- Influence of the diameter of cones

The impact of the cone diameter on the reflectivity is studied by simulating micrometer size cones of constant periodicity (p = 1.5 µm) and height (h = 3.5 µm) and whose diameter is varied from 1 to 2.08 µm. A normal incidence is considered. The simulated reflectivity of these structures is shown in Fig. 3. It appears that at constant periodicity the reflectivity decreases with increasing the cone diameter while the diameter is lower than the periodicity. The curve slope decreases from the point where the bases of the structure are in contact. The large reduction of the reflectivity before this point can be understood by the large reduction of the planar surface between the cones. Then the cone bases start to overlap. Before the planar surface disappears completely, the reflectivity starts to increase slightly, which can be explained by the reduction of the angle between the incident field and the normal of the cone lateral surface, and by the induced reduction of the cone aspect ratio. We observe that the lowest reflectivity is obtained for a cone diameter approximately 30% larger than the structure periodicity. Decreasing the cone periodicity is also recommended for lower reflectivity.

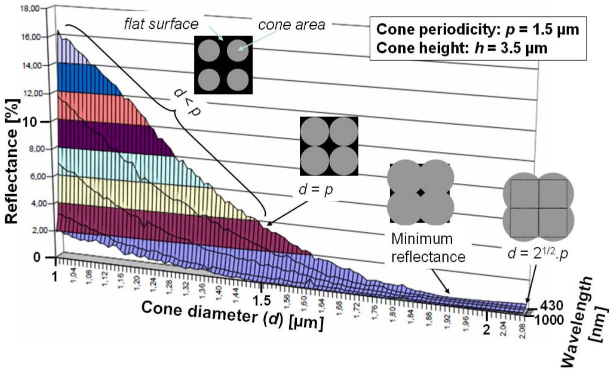

Figure 3: Cone width influence on simulated reflectivity.

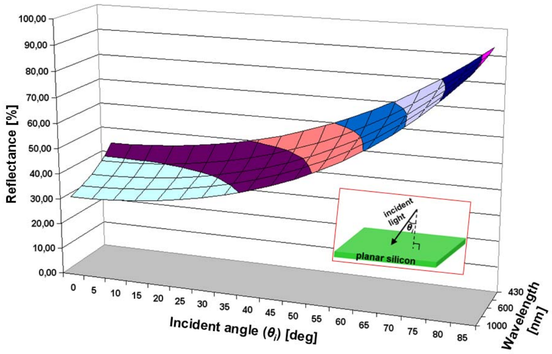

Figure 4: Simulated reflectivity of planar silicon surface with respect to the electric field incident angle.

- Influence of the incident electric field angle

Since promising results on the physical parameters of silicon conical structures for the lowest reflectivity are found as above, textured surfaces consisting of micrometer and sub-micrometer cones with high steepness and high density are simulated to study the variation of the reflectivity with respect to the incident field direction. Fresnel's equation (1) is used as a reference for the variation of the incident field in a theoretical polished surface silicon wafer.

$$R_s(\lambda)=\left(\frac{n_1(\lambda)\cos\theta_i-n_2(\lambda)\sqrt{1-\left(\frac{n_1(\lambda)}{n_2(\lambda)}\sin\theta_i\right)^2}}{n_1(\lambda)\cos\theta_i+n_2(\lambda)\sqrt{1-\left(\frac{n_1(\lambda)}{n_2(\lambda)}\sin\theta_i\right)^2}}\right)^2 \quad (1)$$

where R_s is the *s*-polarized reflection coefficient, λ is the wavelength, n_1 and n_2 are the refraction index of vacuum and silicon respectively, θ_i is the incident field angle from the normal incidence. Simulations are performed with the variation of θ_i from 0° to 85° on a planar (Fig. 4) and textured (Fig. 5) silicon surface.

The periodicity, diameter and height of sub-micrometer cones are 150 nm, 190 nm and 910 nm respectively. As shown in Fig. 5, high density cones exhibit a low reflectivity in the visible range for incidence angles up to 50° from the normal of the surface. A similar effect is observed for the micrometer size structures whose dimensions are presented in Fig.3.

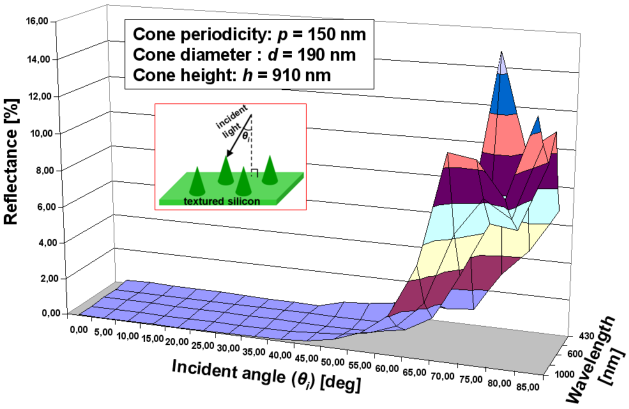

Figure 5: Example of simulated reflectivity with respect to the electric field incident angle.

EXPERIMENTS AND RESULTS

Fabrication

Based on the simulation results presented above, we performed an experimental study of black silicon fabrication and characterization. The black silicon was obtained by using O_2-SF_6 cryogenic deep reactive ion etching on 4 inch polished (100) silicon wafers. By varying the process parameters such as bias voltage, temperature, gas pressure and RF power, we can obtain various structure geometries [11]. The wafers were subjected to DRIE at cryogenic temperatures without any mask. SF_6 gas generates F^* radicals for chemical etching of silicon leading to volatile SiF_4 whereas O_2 gases produce O^* radicals for silicon sidewall passivation with $Si_xO_yF_z$. Such wafers were treated under different plasma conditions in order to obtain different textures of black silicon. Guided by the simulation results, we attempted to obtain the best compromise between density, periodicity and aspect ratio of the silicon cones.

Characterizations

The surface morphologies of black silicon were investigated by scanning electron microscopy (SEM). While the ideal structure geometry discussed in the previous section was difficult to achieve experimentally, high-density of conical black silicon with very low reflectivity was obtained. The cones have base diameter of 150 nm, height of 900 nm and periodicity of 260 nm. The diameter and height values were directly extracted from side-view SEM pictures (Fig. 6). We can observe two types of textures with different scales on this sample. The cone bases are covered by small peaks of width around 100 nm and height 100 - 400 nm. The Fourier Transform (FT) was performed on the top view SEM to extract the pseudo-periodicity of the cones. As the surface properties of the black silicon are spatially invariant, the FT image is symmetrical to the centre, and Matlab is used to calculate the average intensity of all points at a radius (r) over 360° (2):

$$I_{average} = \frac{\int_0^{2\pi} f(r,\theta)d\theta}{2\pi r} \qquad (2)$$

The radius r associated with the maximum of the azimuthal average corresponds to the image mean periodicity (see Fig. 7).

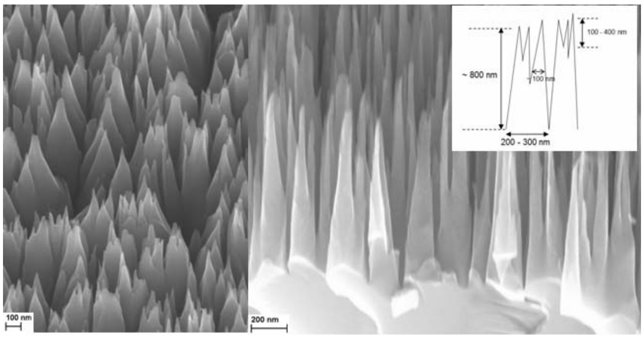

Figure 6: Side-view SEM pictures of the black silicon having the lowest reflectivity. Left: general view. Right: normal view on a cleaved section through the specimen.

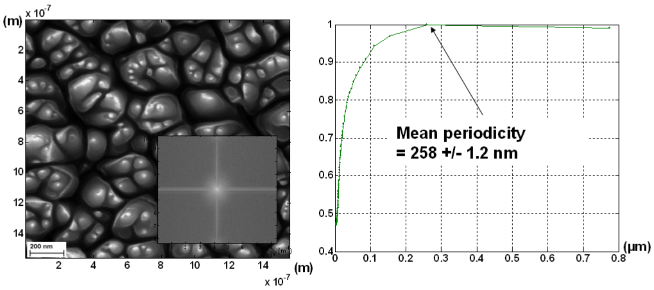

Figure 7: Left: Top view SEM picture of the lowest reflectivity black silicon. (inset: Fourier Transform of the image). Right: Azimuthal average of the FT image.

Reflectance measurements were performed for wavelengths between 400 nm and 1000 nm using a Maya2000-Pro Spectrometer (Ocean Optics), a fiber-coupled halogen light source, and an integrating sphere. NIST reflectivity standards were used for calibration. Fig. 8 plots the measured reflectance in the visible range from planar and DRIE-textured surface under normal incidence. It shows that the black silicon exhibits reflection below 1% from 450 to 830 nm without anti-reflection films. This is the lowest reflectivity published to date for such typical mask-less DRIE black silicon.

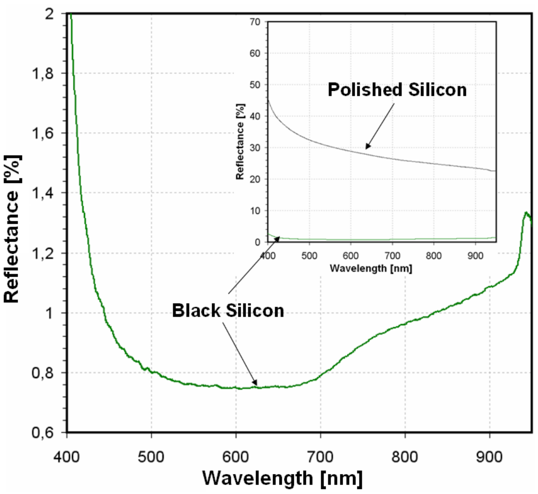

Figure 8: Reflectivity measurement for the lowest reflectivity black silicon surface described in the text, as compared to a polished silicon wafer (inset).

CONCLUSION

To deeply study the influence of the 3D texturization of black silicon on the reflectivity, simulations based on the FEM have been performed. We have simulated the textured structures consisting of cones of sub-micron and micrometer dimensions with different heights and diameters for the optical wavelength. We observed that a black silicon structure with the sharpest and high density cones is expected to obtain the lowest reflectivity. It is obtained when the cones diameter are about 30% larger than the periodicity. Besides, the influence of the direction of the incident field on the reflection of black silicon cannot be neglected. It is shown that angle of the incidence from the normal surface has almost no influence up to 40° on a low reflective surface.

Based on the favorable simulation results, conical black silicon wafer was fabricated by DRIE under cryogenic temperatures with diameter of 150 nm, height of 900 nm and periodicity of 260 nm. The cones are fabricated in a collective manner over the whole wafer area. This structure presents excellent antireflective behavior with a reflectance below 1% in the spectral range of 450 – 830 nm. This reflectance level is the best published in the literature to our knowledge, for black silicon surface obtained by plasma etched method.

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REFERENCES

[1] Howard M. Branz, Vernon E. Yost, Scott Ward, Kim M. Jones, Bobby To and Paul Stradinset, “Nanostructured black silicon and the optical reflectance of graded-density surfaces”, Applied Physics Letters, vol. 94, N° 23, 2009.

[2] M. Y. Shen, C. H. Crouch, J. E. Carey and E. Mazur, “ Femtosecond laser-induced formation of submicrometer spikes on silicon in water”, Applied Physics Letters, vol. 85, N°. 23, 6 December 2004.

[3] B.M.Damiani, R.Lüdemann, D.S.Ruby, S.H.Zaidi, A.Rohatgi, “Development of RIE-textured silicon solar cells”, Photovoltaic Specialists Conference, 2000. Conference Record of the Twenty-Eighth IEEE, 15-22 Sept. 2000, pp.371–374.

[4] H. Jansen *et al*, “The black silicon method. VIII. A study of the performance of etching silicon using SF_6/O_2-based chemistry with cryogenical wafer cooling and a high density ICP source,” Microelectronics Journal, vol. 32, pp. 769-777, 2001.

[5] Z. Huang *et al*, “Microstructured silicon photodetector”, Applied Physics Letters, vol. 89, N° 033506, 2006.

[6] Ali Serpengüzel *et al*, “Luminescence of black silicon”, Journal of Nanophotonics, vol. 2, N° 021770, 2008.

[7] Tommaso Baldacchini *et al*, “Superhydrophobic Surfaces Prepared by Microstructuring of Silicon Using a Femtosecond Laser”, Langmuir, vol. 22, pp. 4917-4919, 2006.

[8] M.Halbwax *et al*, “Micro and nano-structuration of silicon by femtosecond laser: Application to silicon photovoltaic cells fabrication”, Thin solid films, Vol. 516, issue 20, pp. 6791-6795 (2008).

[9] R. Petit,Ed., “Electromagnetic Theory of Gratings”, Berlin, Germany : Springer-Verlag,1990.

[10] E. Richalot, M. Bonilla, M.-F. Wong, V. Fouad-Hanna, H. Baudrand, J. Wiart, “Electromagnetic Propagation into Reinforced -Concrete Walls”, IEEE Trans. Microwave Theory Tech., Vol. 48, No. 3, March 2000, pp.357-366.

[11] R. Dussart *et al*, “Silicon columnar microstructures induced by an SF_6/O_2 plasma,” Journal of Physics D: Applied Physics, 38, 3395, 2005.

CONTACT

* P. Basset, p.basset@esiee.fr