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Obtaining a colored nanostructured layer of amorphous silicon by etching in chlorine-containing plasma

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It is shown that in the self-forming mode in the plasma etching process of amorphous silicon structures (α-Si)/SiO$_2$/Si and (α-Si)/Pt/SiO$_2$/Si in chlorine-containing plasma (Cl$_2$/Ar), it is possible to obtain a multicolored surface from nanoconus and nanowire structures of α-Si. The mechanism of formation of such structures during plasma chemical etching is discussed. The reflection spectra of colored films are given. The bright colors of the surface are caused by the resonant reflection of light in the layers of nanoconus and nanowire structures of α-Si with a sublayer of α-Si nanometer thickness.

Keywords: color, nanostructures, amorphous silicon, plasma etching, nanowire, reflection spectra.

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Nanowire (NW) and nanocone (NC) silicon structures feature unique optical and sensor properties and are used to construct solar cells, optical filters, photodetectors, and gas sensors [1–5]. Disordered NW and NC structures with strong light absorption in the visible range („black silicon") may be obtained by self-assembly with the use of plasma etching [2,6,7]. Multicolored surfaces formed by ordered nanopillar or nanodisk Si structures are often prepared using lithography and etching [1,5,7–9]. Coloration is attributable in this case to the process of resonance reflection of light from an ordered array of silicon nanostructures. Colored surface nanostructures may also be formed in a two-stage process of etching/deposition of Si in fluorine-containing plasma [10]. Owing to its simplicity, the method of formation of NW and NC structures in the process of self-assembly in plasma appears advantageous [11,12]. It is demonstrated in the present study that a bright multicolored surface formed by NW and NC α-Si structures may be obtained by self-assembly in the process of etching of α-Si/SiO$_2$/Si and α-Si/Pt/SiO$_2$/Si structures in Cl$_2$/Ar plasma.

Experiments were performed in a dual-chamber high-frequency ($f = 13.56$ MHz) induction discharge plasma reactor. The design of this reactor was detailed in [13]. Plasma was generated in a quartz discharge chamber and spread into a reaction metal chamber (300 mm in diameter and 300 mm in height), where a high-frequency (HF) electrode was positioned. An anodized Al plate was mounted on the electrode, and samples were positioned on this plate. A certain HF power from a separate generator ($f = 13.56$ MHz) was fed to the electrode to control the ion energy.. The ion energy was set by the emerging self-bias potential U_{sb} [13]. The samples were oxidized (the thickness of SiO$_2$ was 980 nm) Si wafers with a 350-nm-thick layer of amorphous silicon formed by magnetron deposition (samples No. 1) or oxidized Si wafers with Pt (100 nm) and α-Si (990 nm) layers, which were also formed by magnetron deposition (samples No. 2). Samples Nos. 1 and 2 were $\sim 9 \times 9$ mm in size. They were cut out of standard oxidized Si (100) wafers 100 mm in diameter, which were coated first with α-Si or Pt and then with α-Si.

The rate of α-Si etching was determined by laser-interferometry. A He–Ne- laser beam ($\lambda = 633$ nm) was directed at the sample surface, and the reflected signal was recorded by a photodetector and sent to a computer via an interface card. The etching rate was determined by measuring the duration of an interferometer pattern period within which 75 nm of α-Si ($d = \lambda/2n$) were etched away. The refraction index of α-Si was 4.2. A typical interferometer pattern is shown in Fig. 1, *a*. The process of etching commenced at point t_0 and ended at t_{end}, when the signal ceased to vary.

The surface morphology after plasma treatment was examined with a Supra 40 (Carl Zeiss) scanning election microscope (SEM). The reflection spectrum in the visible range was measured with a Leitz MPV-SP spectrophotometer.

The experimental conditions were as follows: pressure $P = 0.6$ Pa; power fed to the inductor $W_{ind} = 800$ W. The flow rates of Ar and Cl$_2$ were kept equal at 25 sccm. The HF bias power varied within the range from 0 to 20 W.

Differently colored surfaces were obtained by sample etching at a low ion energy ($E_i < 100$ eV). When exposed to atmospheric air after etching in Cl$_2$/Ar plasma at an ion energy of ~ 70 eV (the corresponding interferometer pattern is shown in Fig. 1, *a*), the surface of sample No. 1 became multicolored (see Fig. 1, *b*; a color version of the figure is provided in the online version of the paper). High-aspect-ratio nanocone structures were observed on this surface (Fig. 2, *a*). SEM images revealed that differently colored regions of the surface featured equally uniform arrays of nanocone structures with a height varying from 100 to 250 nm and a density of $2.3 \cdot 10^{10}$ cm^{-2}. The tips

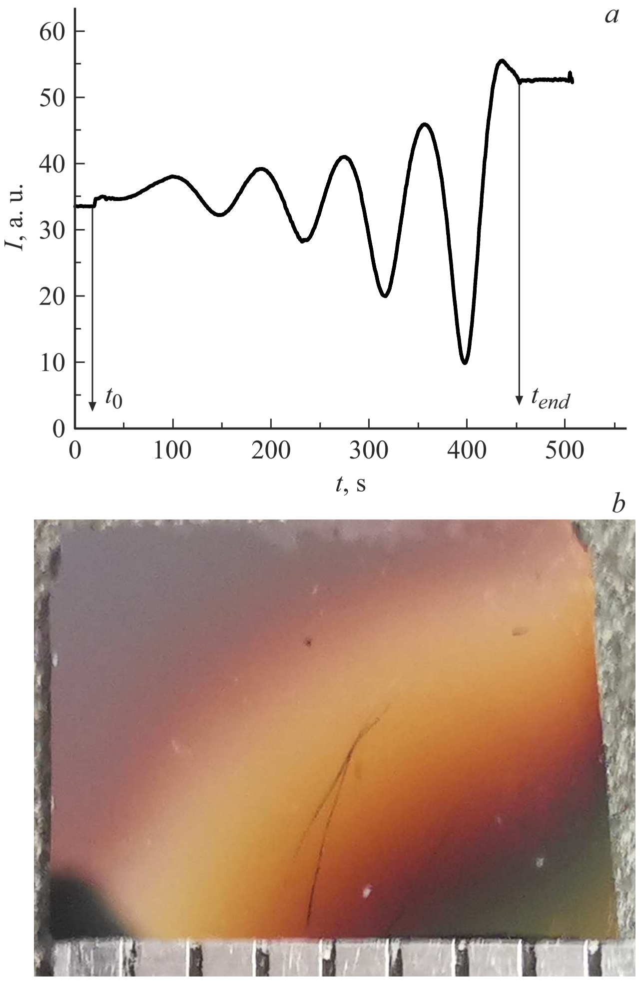

Figure 1. *a* — Interferometer pattern of etching of an α-Si/SiO$_2$/Si sample in Cl$_2$/Ar plasma; *b* — image of the multicolored nanostructured surface of a sample with NC α-Si structures (a color version of the figure is provided in the online version of the paper).

of nanocones were 10–20 nm in size, and the width of their bases was 40–50 nm. Since the α-Si film was not completely etched away, an α-Si underlayer remained at the base of nanocones. Thickness h of this underlayer (Fig. 2, *a*) increased linearly from approximately 30 to 90 nm along the cleavage line from the left edge to the right (along the scale in Fig. 1, *b*). Different surface colors corresponded to different thickness h values.

It is fair to assume that surface colors change not due to variations in diameter, height, or density of nanocones, which remained roughly equal, but due to thickness variations of the unetched α-Si layer. Although the color of a structured surface is known to be specified by the diameter of nanopillar structures, it is defined in the present case mostly by the interference of light in the α-Si underlayer of a varying thickness. The influence of an additionally deposited dielectric layer on the resonance reflection of α-Si has been noted in [14]. The color of such an NC surface did not change with viewing angle. This is a characteristic feature of a structured colored surface of this kind [7,14]. It may be noted that the surface loses its bright coloring if nanocone structures are erased mechanically.

The formation of nanocones in the process of etching of α-Si in Cl$_2$/Ar plasma is attributable to three factors: the presence of a natural nonuniform nanometer-thick SiO$_2$ layer on the surface, the high anisotropy of α-Si etching, and the high selectivity of etching of α-Si relative to SiO$_2$. It was found experimentally that the α-Si/SiO$_2$ selectivity of etching in chlorine-containing plasma exceeded 1000 at a low ion energy (< 60 eV). Since the natural oxide film on the sample surface had a nonuniform thickness, a nanomask in the form of SiO$_2$ islands emerged in the process of its etching. Nanocones form as a result of anisotropic etching of α-Si through this SiO$_2$- island nanomask.

A similar multicolored sample surface is also obtained if one performs pretreatment of samples No. 2 and removes the natural oxide film from them in chlorine-containing plasma at a high ion energy. A thin SiOCl$_x$ layer then formed on the surface, and the α-Si layer with a thickness of ~ 230 nm was etched at a lower ion energy ($U_{sb} = -44$ V, $W_{sb} = 10$ W). The amplitude of the interferometer signal decreased with time in this case. This indicated that the etching of α-Si proceeded with the formation of more closely packed nanostructures (Fig. 2, *b*). The formation of a denser array of high-aspect-ratio NW structures may

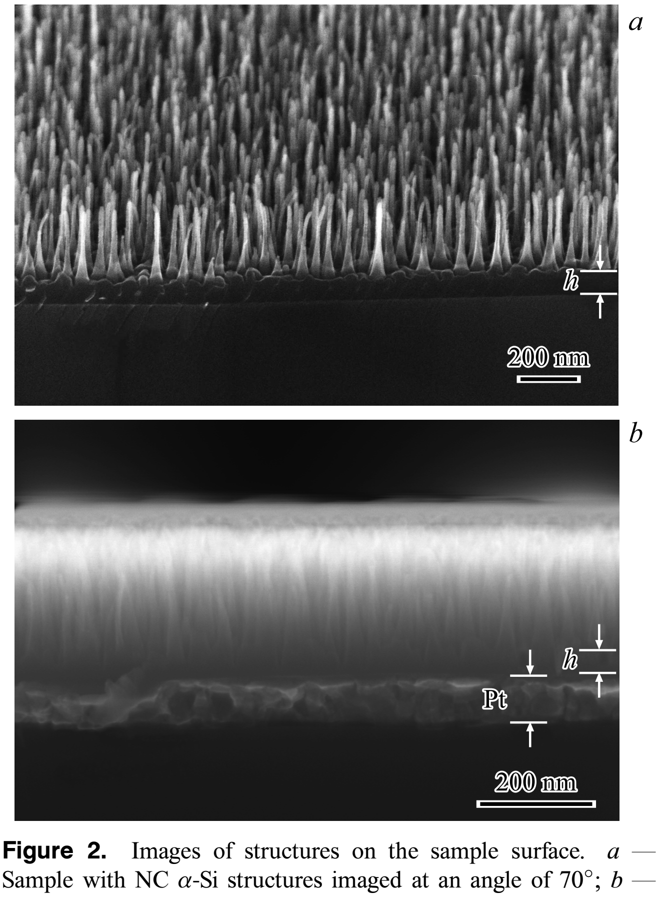

Figure 2. Images of structures on the sample surface. *a* — Sample with NC α-Si structures imaged at an angle of 70°; *b* — NW α-Si structures on the cleaved face of an α-Si/Pt/SiO$_2$/Si sample.

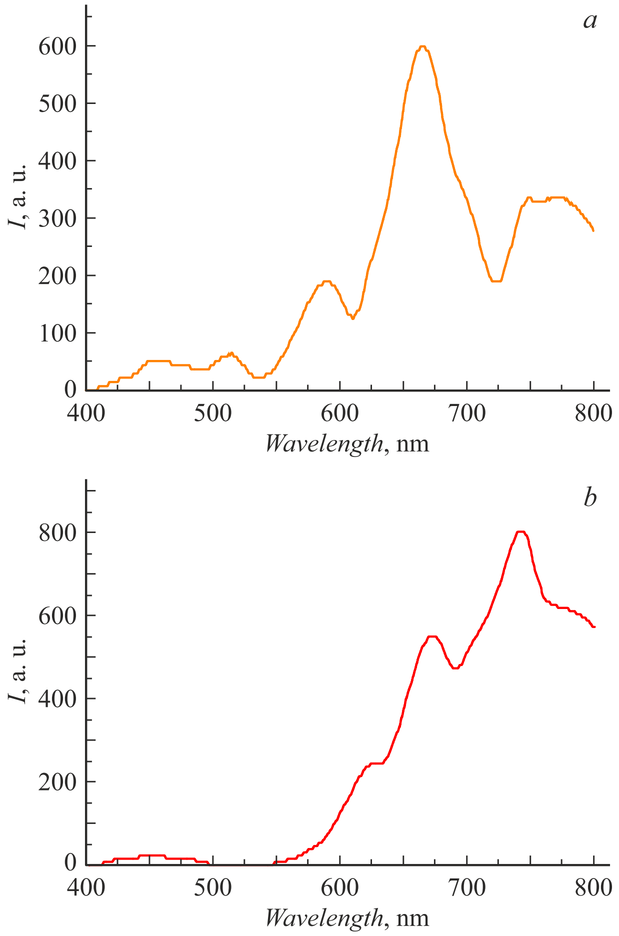

Figure 3. Surface reflection spectra of samples α-Si/SiO$_2$/Si with NC structures in the orange region (a) and α-Si/Pt/SiO$_2$/Si with NW structures in the red region (b).

be attributed to the fact that α-Si is etched through a SiOCl$_x$ mask, which features smaller nonuniformities than the natural SiO$_2$-layer mask. The structures forming on the sample surface in this case are closer in shape to nanowires than to nanocones. Their tips were smaller than 20 nm in size, and nanowires with a height of ~ 250 nm were often attracted to each other. The density of nanowires was $\sim 5 \cdot 10^{10}\,\text{cm}^{-2}$. Just as in the first case, the surface coloration depended on the presence of an α-Si underlayer. Its thickness varied over the surface from 10 to 40 nm. Since colored NW structures formed on the metal surface, it is fair to assume that SiO$_2$ did not exert a significant influence on coloration in the first case. Figure 3 shows local reflection spectra of sample No. 1 in the orange region (a) and sample No. 2 in the red region (b). Similar reflection spectra were observed for a Si surface structured with nanodisks and an interference SiO$_2$ sublayer [14]. The emergence of small local peaks in the spectrum may be attributed to the presence of NW structures of different thickness in the array.

The presented method for production of a colored α-Si surface may be used in fabrication of various photonic and sensor devices.

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Conflict of interest

The authors declare that they have no conflict of interest.

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