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Silver nanoparticles assisted etching of silicon

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Silicon nanostructures are attractive for optics and optoelectronics application to provide more efficient light absorption. Most common processes for formation of silicon surface nanostructures are rather expensive and require high temperatures, high vacuum and hazardous precursors. The silver nanoparticles assisted electroless etching process is a simple and cheap method for preparation of nanostructured silicon surfaces. The silver nanoparticles are deposited in-situ by electroless deposition from non- HF (Hydrofluoric acid) containing solution of activated persulfate. Silicon is selectively etched in HF based solutions with the help of silver nanoparticles. Both the etch process and the deposition of silver particles are studied. The experimental observations are used to get more insight into the etching mechanism.

Keywords: silver nanoparticles, activated persulfate, silicon, wet-chemical etching

INTRODUCTION

Recently, [1-7] new methods for a nano-scale isotropic texturing of silicon surface based on metal particles (Au, Ag, Pt) catalyzed wet chemical etching have been developed. These methods are using an electroless process for texturing and therefore, are suitable for mass fabrication of nano structures on the silicon surface. A metal-assisted electroless etching using $Na_2S_2O_8$ as an oxidizing agent in a HF containing aqueous solution was proposed [8, 9] to form a porous silicon surface layer on a highly resistive p-type single crystalline silicon. A thin layer of Ag or Pd was deposited onto the Si surface before the immersion in the $HF/Na_2S_2O_8$ solution. This technique was further modified [10] to fabricate silicon nanowires on silicon in aqueous $HF/(AgNO_3+ Na_2S_2O_8)$ solution. The targeted application of these techniques was the photoluminescence enhancement [11].

In this paper, the development of rapid surface nanotexturing technique consisting on two-stage wet chemical process, which is suitable for all types of crystalline silicon substrates and surface morphologies, is presented. The nanotexturing technique includes an electroless treatment in aqueous solution of silver ions activated sodium (potassium) persulfate for local oxidation/ reaction on the silicon wafer surface following by oxidation/reaction products etching in an aqueous solution of HF and H_2O_2.

Persulfates (especially $Na_2S_2O_8$ and $K_2S_2O_8$) are strong oxidants that have been widely used in many industries. The standard oxidation – reduction potential for the reaction:

$$S_2O_8^{-2} + 2H^+ + 2e^- \rightarrow 2HSO_4^- \qquad (1)$$

is 2.12 V, as compared to 1.8 V for hydrogen peroxide (H_2O_2), which is widely used in the electroless etching of silicon. In addition to direct oxidation, sodium persulfate can be induced to form sulfate radicals. The sulfate radical is one of the strongest aqueous oxidizing species with a redox potential estimated to be 2.6 V, similar to that of the hydroxyl radical, 2.7 V. In addition to its oxidizing strength, persulfate and sulfate radical oxidation have several advantages over the other oxidant systems. First, they are kinetically fast (when appropriately activated). Second, the sulfate radical is more stable than the hydroxyl radical.

Reactions involving persulfates (persulfate ions) usually are slow at ordinary temperatures. There are, however, several well-developed methods [12] to activate/ catalyze the persulfates such as transition metal ions presence, heat, or hydrogen peroxide addition, for instance. In the transition metal (metal ion) activation, the following reaction is performed through the metal salt initiation (for example, readily water-soluble silver salt – $AgNO_3$) and persulfate [13]:

$$Ag^+ + S_2O_8^{-2} \rightarrow Ag^{2+} + SO_4^{\bullet -} + SO_4^{-2} \qquad (2)$$

Ag^{2+} is a highly reactive transition ion while SO_4^{2-} and $SO_4^{\bullet -}$ - sulfate radical are known as

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powerful oxidants. All these species are capable to interact with the silicon surfaces causing local oxidation/ surface reactions, the exact mechanisms and the reaction products being still not clear [14].

EXPERIMENTAL DETAILS

Multi-crystalline as well as single crystalline (100) p –type silicon wafers with resistivity of 0.5-2 Ω.cm and 0.5-3 Ω.cm respectively were used as substrates. All samples were first cleaned using the standard procedures. The saw damage (SD) of multi-crystalline (mc-Si) wafers was removed by treatment in an isotropic etching/texturing solution (HCl: HF: HNO_3 = 11:2:7 at 10 °C) or by polishing etching in NaOH (50%): H_2O = 1:1, for 3 min at 80 °C. Single-crystal silicon (c-Si) wafers were textured with random pyramids using the standard KOH/IPA etching method. For a nanotexture preparation on the wafer surfaces the samples, after SD removal, were first immersed in mixed $Na_2S_2O_8$ ($K_2S_2O_8$) / $AgNO_3$ aqueous solution for electroless selective oxidation/reaction. The electroless solution was prepared as follows: an aqueous solution of silver nitrate in dilute nitric acid was first prepared then solid sodium/ potassium persulfate powder was added to the liquid. When this is done, the liquid becomes lightly brown. The brown color is presumably due to silver (III) ions. In acidic media, persulfate is capable of oxidizing silver (I) ions to silver (III) ions according to the following reaction [15].

$$Ag^+ + S_2O_8^{2-} \rightarrow Ag^{3+} + 2SO_4^{2-} \quad (3)$$

$$Ag^{3+} + Ag^+ \rightarrow 2Ag^{2+} \quad (4)$$

Silver (III) ions are not very stable. This liquid slowly loses its color and releases oxygen. A black precipitate of silver (I) silver (III) oxide was formed. The solution was finally filtered and then ready for use.

After the electroless treatment, an etching in H_2O, H_2O_2 (35%) and HF (40%) solution was performed. Different concentration ratios of the electroless and the etching solutions as well as different immersion/ etching times (ranging usually from 5 to 20 min for electroless treatment and from 1 to 10 min for etching) were used. The nanotexturization was performed at room temperature (RT) and under ambient light. The porous silicon layer formed especially after longer etching was removed of some wafers in diluted KOH solution. Finally, both wafer cleaning and metal ions/particles removals were done consequently, in concentrated HNO_3 (at RT) and standard HPM (HCl: H_2O_2: H_2O = 1:1:5; at 80°C for 20 min) solutions.

The total reflectance of the texturized wafers was measured with a Hitachi U-3010 spectrophotometer equipped with an integrating sphere, in the wavelength range 300-900 nm. The wafers surface morphology was studied by using Scanning Electron Microscopy (SEM) and Scanning Force Microscopy (SPM) techniques. For SEM (JEOL JSM-6500F) and SPM measurements square pieces of 20 x 20 mm^2 size were prepared using laser cutting.

RESULTS AND DISCUSSION

The surface of silicon after an electroless treatment in $Na_2S_2O_8$ (SPS)/ $AgNO_3$ (AN) solution was loaded with particles as shown in Fig. 1. The size and the shape of the particles depend on the immersion time. On the silicon surfaces treated for 20 min (Fig.1a) in above mentioned solution randomly distributed isolated nearly spherical particles are obtained. Most of the particles were of several tens of nanometers although the observed size distribution was broad probably due to particles aggregation up to μm dimensions. Silver and in some larger particles oxygen were detected by EDX (Energy Dispersive X-ray spectrometry) analyses (Fig.1b). The same analyses of the surfaces not covered with particles show mainly silicon and small quantity of oxygen. It could be supposed that the particles are probably silver metal nanoparticles or/and silver oxide particles. The surface of the silicon is also covered (at least partially in selected areas) with an oxide layer. The surface changed from hydrophobic initially (after a HF dip) to hydrophilic after the above electroless treatment.

Since no porous layer was formed neither hydrogen evolution was observed during the electroless immersion treatment we suppose that the reactions between Si and the strong oxidant containing SPS/AN solution, (whose most reactive species are sulfate radicals and Ag^{2+} ions, see eq. 2) lead to oxidation of silicon and silver nanoparticles/silver oxide particles deposition.

The SO_4^{-} radical anion is an extremely strong electron acceptor. It extracts an electron from the VB (valence band) of silicon, this is equivalent to a hole injection into the VB

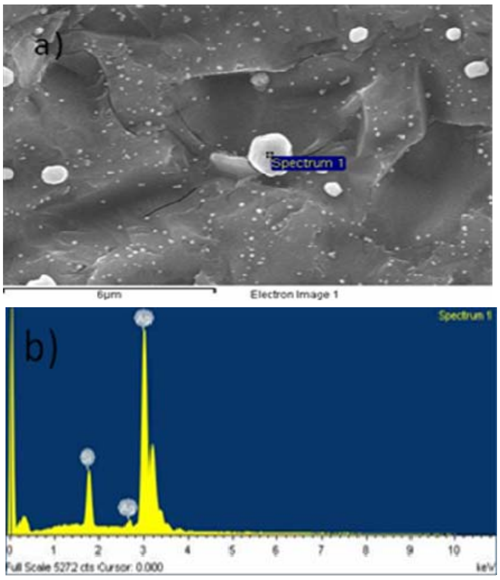

Fig. 1. Silver nanoparticles deposited onto silicon surface plan-view SEM image, scale bar – 1µm (a). EDX analyses (b) of a silver nanoparticle.

$$SO_4^{\cdot -} \rightarrow SO_4^{2-} + h^+_{(VB)} \qquad (5)$$

Therefore, after the electroless treatment of the silicon surfaces in SPS/AN solution the surfaces became oxidized with randomly distributed silver oxide particles and metal Ag nanoparticles.

Silicon wafer surfaces etching for nanotexturization was performed in a $HF/H_2O_2/H_2O$ solution. After an initial short period (approximately 60- 90sec) in the etching solution gas (H_2) release was observed and the silicon surface became visible darker. The initial period is most probably necessary for the silicon oxide/reaction products dissolution.

Ag^+ reduces onto the Si wafer surface by injecting holes into the Si valence band and oxidizing the surrounding lattice. The Ag nuclei adhered to the silicon surface possess higher electronegativity than Si and, therefore, strongly attract electrons from Si to become negatively charged. These Ag nuclei have strong catalytic activity and could provide an appropriate surface for the reduction of Ag ions. The Ag^{2+} and Ag^+ ions on the silicon surface get electrons from Ag nuclei to be deposited around them, rather than on bare silicon. In this way, the Ag nuclei grow into larger particle (see Fig.1 b) as more Ag ions are deposited [15].

$$Ag^{2+} + e^- \rightarrow Ag^+ \qquad (6)$$

$$Ag^+ + e^- \rightarrow Ag \qquad (7)$$

Then the reaction proceeds as a localized microscopic electrochemical process consisting of H_2O_2 reduction at the silver particles sites and dissolution of silicon into H_2SiF_6 at the wafer surface described by the following overall chemical process [15]:

$$Si + 6HF + n/2H_2O_2 \rightarrow H_2SiF_6 + nH_2O + [(4-n)/2]H_2 \qquad (8)$$

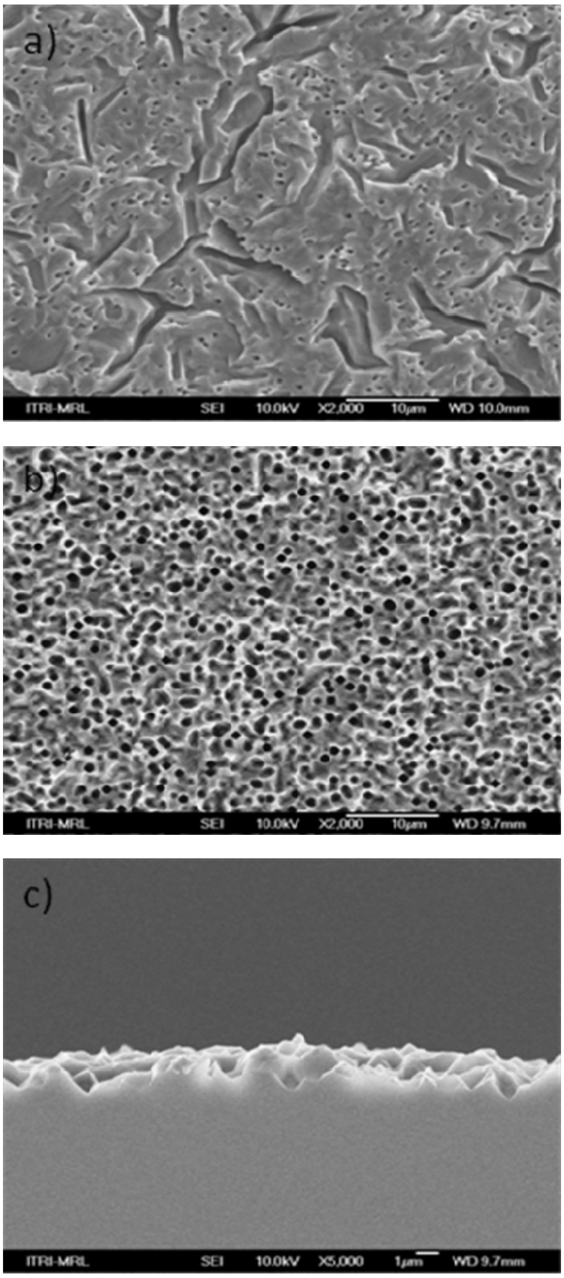

Fig. 2. Plan-view SEM images (tilted 45º). Morphologies of the silicon surfaces: multicrystalline silicon after SDR (a); multicrystalline silicon after silver nanoparticles-assisted etching (b) and cross-sectional SEM of silver nanoparticles-assisted etched multicrystalline silicon surface (c), Scale bars – 1µm.

Fig. 2 (a,b) shows SEM surface morphology images of a mc-Si wafer after acidic SDR and after nanotexturization with SPS/ AN electroless treatment and etching in H_2O: H_2O_2: HF = 10:5:1 solution. In comparison to the SDR surface rather uniform texture with smooth surface features possessing lateral size less than 500 nm was observed in the nanotextured wafers. The reflection suppression obtained after the nanotexture formation on silicon wafers according to the present method can be understood further from the morphology of the etched surface as revealed by SPM measurements (SII/SPI 3 800N, Seiko Instrument). The micrograph on Fig.3 shows densely packed hillocks with relatively rounded shape. The etching time in H_2O: H_2O_2: HF = 10:5:1 solution was 6 min. Usually the reflectivity decreases with the RMS (root mean square) surface roughness and the aspect ratio (depth to the lateral size ratio) values. P-V (peak-to- valley, maximum height difference) represents the difference between the highest point and the lowest point of a designated surface. In all samples, these dimensions are of several hundreds of nanometer scale – i.e. the surface is nanotextured. Some of the parameters relevant for the texture estimation of mc-Si samples prepared by electroless immersion in SPS 0.1M: AN 0.1M solution with volume ratio 10:1 and 20:1 respectively are listed as follows: RMS 47nm -57 nm; P-V 321nm -383 nm; aspect ratio 1.86-2.07. It is obvious that all the measured parameters (RMS, P-V and the aspect ratio) increased for the silicon surfaces treated with higher SPS content electroless solution. The estimated etching rate increases from approximately 53nm/min to 64 nm/min as the sodium persulfate concentration in the electroless solution increases.

A porous layer on the surface of the mc-Si wafer, pre-textured with an alkaline solution for SDR, was formed after nanotexturization using 10 min SPS/AN electroless immersion and 2 min etching in H_2O: H_2O_2: HF = 10:5:2 solutions as seen in Fig.4a. The surface morphology represents crystalline facets of approximately 1 μm size. The porous layer was completely etched back after a treatment in diluted KOH solution (Fig.4 b).

Fig. 5 shows the total reflectance spectra of c-Si (pyramids pre-textured) surface as well as the c-Si surface after nanotexturization using an electroless selective oxidation treatment in $K_2S_2O_8$ (PPS)/$AgNO_3$ (AN) solution in a volume ratio of 20:1 for 6 minutes and etching in H_2O: H_2O_2: HF = 10:5:1 solution for 6 minutes. After the

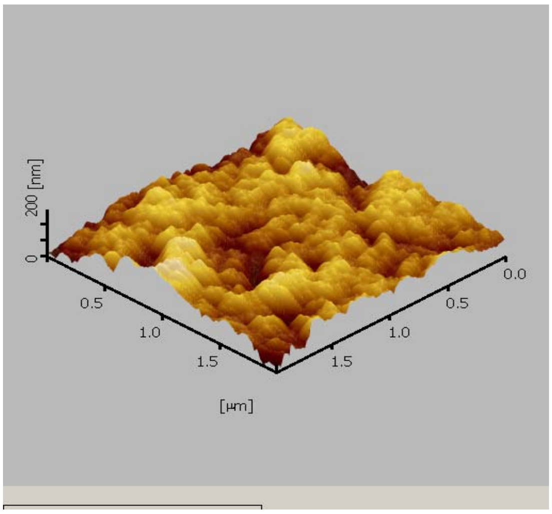

Fig. 3. SPM profile of nanotextured silicon surface.

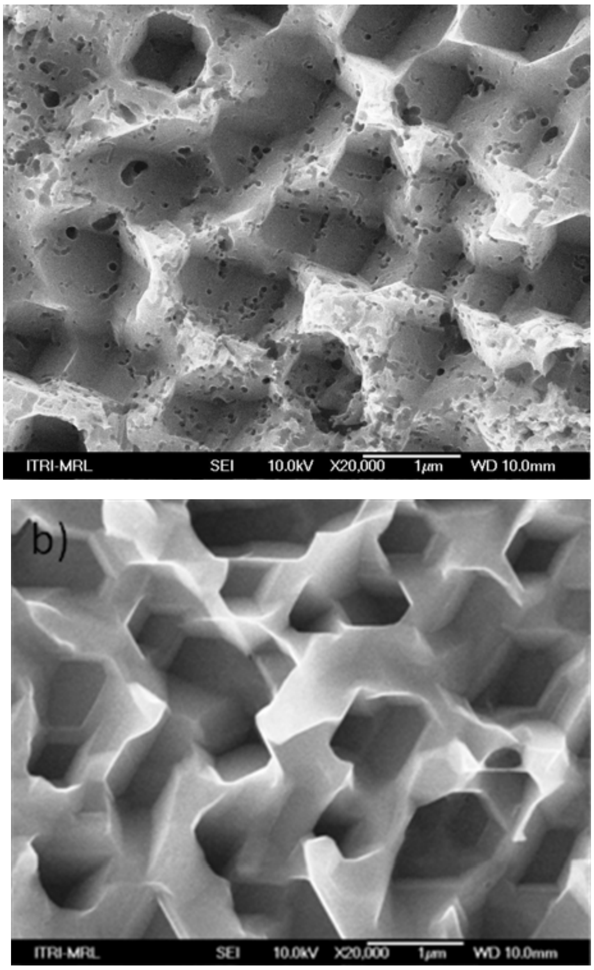

Fig. 4. SEM plan view images of alkaline pre-etched Si surface after nanotexturization (a) and after the surface porous layer removal (b), Scale bars – 1μm.

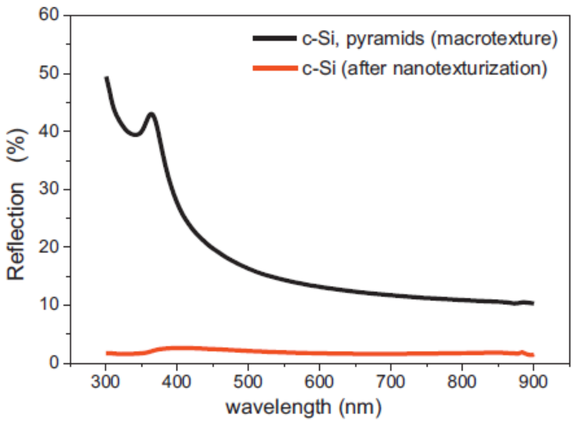

Fig. 5. Reflectance spectra of c-Si wafers after standard pyramids etching and after an additional nanotexturization.

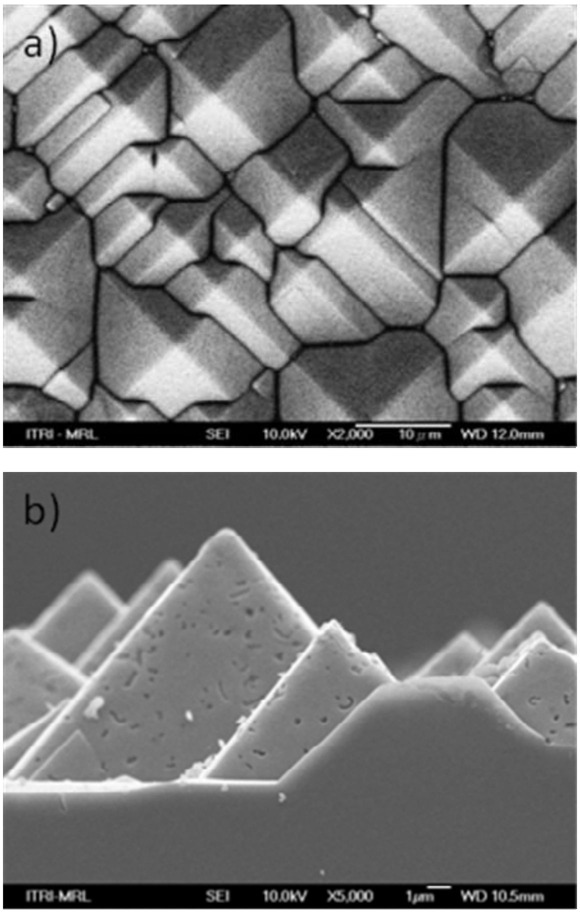

Fig. 6. SEM plan-view image of silicon micro/nano surface structure, scale bar – 10 µm (a) and cross-sectional image (b), scale bar-1 µm.

nanotexturization the reflectance decreased to less than 5% in the whole measured wavelengths interval from 300 nm to 900 nm. It is obvious that the nanotexturization method according to the present research is equally effective on both mc-Si and c-Si substrates as well as on macrotextured (rough) and polished surfaces (not shown). Especially interesting from the practical applications point of view is the possibility to prepare two scales texture [16], i.e. nanotexture on top of a macrotexture as in the case of pyramids pre-textured sc-Si as shown in Fig. 6 (a, b). In these hierarchically textured surfaces additional functionality as superhydrophobicity could be achieved.

CONCLUSIONS

A simple wet chemical method for nano-scale texturization of silicon surface is proposed. The method applied on mc-Si as well as c-Si resulted in significant reflectance suppression in a broad spectral range. The method is applicable for various of silicon surface morphologies and combined micro/nano hierarchical structured surfaces are easily prepared allowing additional surface functionality. The method is further potentially applicable for surface structuring of other semiconductor materials.

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ЕЦВАНЕ НА СИЛИЦИЕВИ ПОВЪРХНОСТИ С ПОМОЩТА НА СРЕБЪРНИ НАНОЧАСТИЦИ

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(Резюме)

Наноструктурирането на силициеви повърхности е от съществено значение за приложения в оптиката и оптоелектрониката с цел осигуряване на по ефективна абсорбция на светлината**.** Повечето от известните досега методи за получаване на наноструктури върху повърхността на силиций са сравнително скъпи и изискват високи температури, вакуум и опасни за здравето химикали. Методът за безтоково ецване с помощта на сребърни наночастици е доказано по-лесен за практическо изпълнение и с по ниски финансови разходи. Сребърните наночастици са отложени непосредсвено върху повърхността на силиция чрез третиране в разтвор на активиран персулфат, който не съдържа флуороводородна киселина. Силиция е ецван селективно след това в разтвор на флуороводородна киселина и водороден прекис с помощта на отложените сребърни наночастици. Механизъма на отлагане на сребърните наночастици както и на ецването на силиция са изследвани.