Microstructuring of silicon crystal surface for solar cell application

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Abstract

In this paper we developed mechano-chemical methods of structuring the surface of crystals Si (100) for use as substrates for solar cells. It was found that from all studied mechanical methods the 'scratching' one is more acceptable and chemical treatment regimen (KOH(10%):H_2O(90%), T=350K) was found to be the most effective for creating the microstructured surfaces.

Key words: chemical treatment, nano/microindentation, Si(100) crystals, surface structurization, various tribology methods

Introduction

Silicon is widely used in the manufacture of integrated circuits, microelectromechanical systems, optoelectronic devices. Today silicon is widely studied in terms of mechanical behavior with purpose of deeper knowledge of the processes that occur under mechanical actions in the process of manufacture and operation of devices based on it. In recent years more attention is paid to change monocrystalline silicon under the action of concentrated load (nanoindentation and microindentation) to create special structures and functional surfaces [1-3].

The structuring of the Si substrate surface is carried out in order to increase the active surface area which in turn serves to raise the efficiency of solar cells based on Si [4]. Frequently the structurization is produced by photolithography or laser texturing assisted by chemical treatment. However, these methods are expensive and time consuming to obtain special relief surfaces. It requires the application of additional research to find new technologies faster and less expensive.

In view of the above, in this paper the problem of raising the efficiency of solar cells based on Si has been focused on using technology to produce the surface microstructures by micromechanical deformation prior to subsequent chemical treatment.

Experimental

Nanoindentation technique was used to local deformation of Si, plane (100), the n-type doped with phosphorus and having resistivity of 4.5 Ωcm. To perform local deformation the Nanotester PMT3-NI-02 and microhardness tester PMT-3 devices were used. The Nanotester apparatus PMT3-NI-02 is equipped with Berkovich trihedral diamond pyramid (the angle between the side and axis is 65°). The dynamic nanoindentation method is conducted no "post factum", as it takes place in case of quasistatic microhardness testing, but observing the dynamic load by recording deepening indenter into the material tested [5]. The quasistatic microindentation was performed with Vickers indenter, the angle between the sides α = 136 °. Loads applied to the indenter varied from P = 0.01N up to P = 0.5 N.

To create the active microstructuring surface of semiconductor materials with subsequent application in solar cells, a special mechanical and chemical techniques have been applied: sclerometric nanoindentation ("scratching"), "imprinting", blasting, various tribological regimes in combination with selective chemical treatment. Detection the fine structure of the material under study was performed using light microscopy (LM) (Amplival, XJL-101, MII4) and atomic force microscopy (AFM). In order to obtain the structured surface, by forming the dislocations and other defects (micro-nanocracks) created in Si single crystals using the above-mentioned methods, the selective chemical treatment with various reactives has been applied (Table).

Given the fact that in Si crystals the dislocations are sedentary (almost fixed) at room temperature, the crystals were exposed to annealing at T = 700°C during 1 h to increase their mobility after plastic deformation.

Table. The chemical composition of reagents and chemical treatment regimes of the Si(100) crystals

Nr	Etchant	Etching time	Tempe-rature
1	1p.$K_2Cr_2O_7$(sol.conc.) + 2 p.H_2O+ 3p.HF	5 s	T_c
2	(25 mg $K_2Cr_2O_7$ +50 ml H_2O)+ 2p.HF	5 s	100°C
3	(25 mg $K_2Cr_2O_7$ +50 ml H_2O)+ 2p.HF	25 s	40°C
4	40%KOH:60%H_2O	5 s	100°C
5	30%KOH:70%H_2O	30 s	100°C
6	20%KOH:80%H_2O	10 min	T_c
7	20%KOH:80%H_2O	10 min	40°C
8	10%KOH:90%H_2O	72 h	T_c
9	10%KOH:90%H_2O	15 min	50°C

Results and discussions

First, using the "scratching" (sclerometric nano- and microindentation), it was investigated the influence of different factors, such as strain rate, the indenter displacement relative to the geometry, the value of the load on the microstructuring mechanism in the deformed zone of monocrystalline silicon with the aim of applying in solar structures.

(i) the influence of the strain rate

Three deformation rates (v), namely 40, 50 and 100 μm/s, were applied on the Si(100) samples, for track production by the sclerometric nanoindentation method. It was found that the deformation at higher speeds creates scratches ("tracks") smooth, without damages. Lower speeds instead form some tracks accompanied by brittle separations of the material. As the most suitable speed for the silica surface structurization was selected v = 50 μm/s, on the one hand, the tracks being more pronounced, on the other hand, free from the fragile damage.

(ii) influence of the indenter moving direction relative to indenter geometry on the track microstucture

To detect the influence of movement direction relative the indenter geometry on the track microstucture two kind of tracks were made: by side of the indenter (Fig. 1a) and by indenter edge (Fig. 1b).

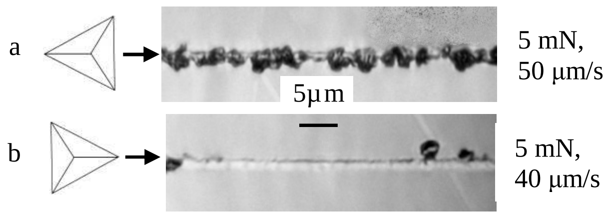

Fig. 1. LM. Shape of tracks created by two methods:
a – by side of indenter; b – by indenter edge

As shown in the pictures, the track from moving pyramidal indenter ´face forth´ is accompanied by more pronounced damages than at the edge deformation (compare Fig. 1a and 1b).

(iii) the influence of load value on microstructuring mechanism of deformed area

The value of the load applied to the indenter is an important factor which can influence the mechanism of deformation processes involving movement of the material at various levels: atomic (interstitial plasticity), dislocation plasticity, phase transfer, discontinuous, brittle fracture. To follow these processes with load increase, tracks with different values of *P, mN*: 3, 4, 5, 6, 7, 8, 9, 10 and 20 were performed on the nanotester and 10, 30, 50 on the microhardness tester.

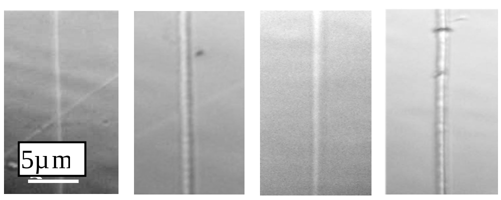

Fig. 2. LM. Images of tracks performed on nanotester with different loads, *P,mN*: 3, 5, 7, 20 (from left to right respectively)

The tracks of nanotester were plotted in parallel rows along the direction <100> (Fig.2) and the number of tracks in the form of parallel lines along the two perpendicilar directions <100> and <110 >, as well, along the <100> direction the tracks were made using the microhardness tester. The load increase leads to the drawing of the destruction mechanism into the track deformed zone. It was shown the damage begin to appear at loads P = 20 *mN* (Fig. 2). This load may be considered critical above which it is not recommended to perform tracks with Berkovich pyramid. Experiments have shown that the tracks made by the Vickers pyramid, having more obtuse tip of angle than the Berkovich one, are no damages up to P = 50 *mN*.

(iv) the track topography influence on the microstructure obtained after chemical treatment

The next phase of investigations consisted into structurization of the zone track surface. It is known [6,7] that the structural defects formed in regions of tension from the surrounding of tracks (scratches) due to the chemical treatment can create a specific three-dimensional structure leading to the modification of reflection degree of the crystal surface, respectively, to improvement of the solar cell volt-ampere characteristics.

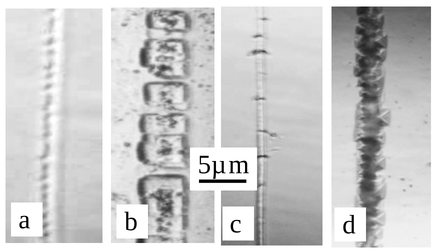

Fig. 3. LM, Si(100). Images of Berkovich tracks before (a,c) and after (b,d) chemical treatment. a,b – 10 mN, 50 μm/s; c,d – 20 mN, 50 μm/s

Reagent 1 (see Tab.) was used to obtain three-dimensional images of chemical treatment around the tracks. The tracks, which were plotted with lower load (10 mN), after chemical treatment form quadrilateral prismatic figures (Fig. 3 a,b), while those deposited by higher load (20 mN) create the inverse quadrilateral pyramids (Fig. 3 c,d).

Tracks formed on the microhardness tester with various loads had slightly another pattern, the rounded prism-shape or the shape of an irregular quadrilateral dimensional inverse semiprism more or less deep, in dependence on the load value (Fig. 4a).

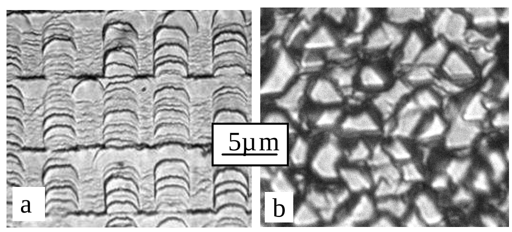

Fig. 4. LM. a – image of tracks, plotted on the Si with Vickers indenter, after chemical treatment (P=10 mN).
b – image of Si surface, deformed by corundum micrograins, after chemical treatment

Tridimensional structures became deeper for tracks made with heavier loads. However, it is characteristic of all the images that they have the form of truncated inverse prisms with the plate base. Similar figures were formed by deformation with micrograins of corundum (Fig. 4b). In addition to the above-described deformation methods, other mechanical means of structurization were applied, such as the arbitrary movement of abrasive paper (sandpaper), unilateral motion along the direction <100 > or <110>, and movements in the form of a grid along the direction <100> and <010>.

The surface pattern obtained by arbitrary moving was studied at first without chemical treatment in reflection and interference regimes of light microscopes. It was found that the depth of the tracks is less than 300 nm. After chemical treatment the surface assumes more pronounced lines formed of point etching pit. Movement of the crystal with a greater force creates a pronounced relief formed of prismatic or oval trudimensional figures preferably oriented in the directions <100>.

(v) selection of the efficient chemical treatment regime for Si surface structuring

Note that the deformed surface topography in various ways, discussed above, and subjected to chemical treatment using reagents 1-7 of Tab. 1 has a common structure characterized by the appearance of three-dimensional spatial inverted trapezoids having irregular arrangement on the surface or orientation <100> (Fig. 4b).

As shown in [6,7] such type of spatial structures fabricated on the Si surface are welcome for solar energy that increase the efficiency of solar cells by about 2% and improve other parameters such as short circuit current density, voltage open circuit, fill factor.

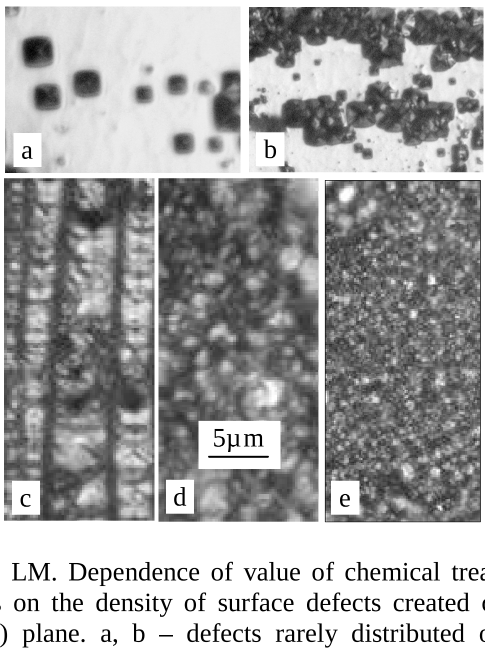

Fig. 5. LM. Dependence of value of chemical treatment figures on the density of surface defects created on the Si(100) plane. a, b – defects rarely distributed on the crystal surface; c-e – defects densely packed as a result of deformation with: c – abrasive paper; d – diamond powder and e – sandblasting. The duration of chemical treatment t = 48 h using the reagent **8**

At the same time, it is expected that the solar cell parameters could be improved in the future by creating spatial structures having the form of inverted pyramids with sharp tip. To this end our research were continued in terms of modification of chemical agents and the treatment regime of deformed silicon surfaces.

After multiple test choices reagent **8** was selected which gave quite right results (Tab.1). In this reagent the concentration of water solution of potassium hydroxide was reduced compared to compositions **4-7**. Now 10% KOH and 90% H_2O was taken for composition **8**.

As a result of crystal treatment with this composition, the etching pits got the shape of quadrilateral reverse pyramids sharp at the top. However, the reaction rate was too low. The rectangles pyramids of tridimensional shape appeared only after over 36-48 hours of chemical attack (Fig. 5). Inverted pyramids still large and well shaped were formed after 72 h chemical treatment (Fig. 6).

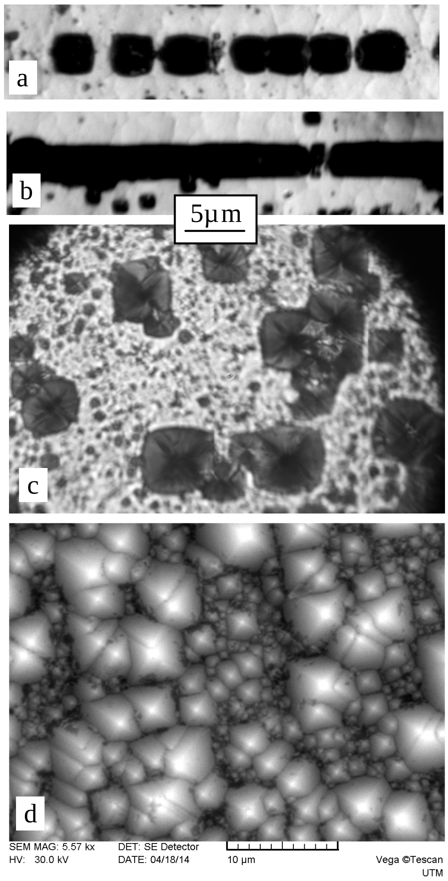

Fig. 6. LM (a-c), SEM (d). Images of etching pits created on the surface of Si (100) crystal by use the reagent **8** of Tab. 1, t = 72 h. Tracks made with P, mN: a - 5; b - 10

The large dimensions have the isolated defects on the crystal surface (Fig. 6 c). But as the density of defects increases, the figure size becomes smaller (Fig. 6 d). This result shows that to achieve maximal effect of efficiency of solar cells it is necessary to establish the optimal density of surface defects on the crystal and to select the final chemical treatment regime.

Spatial structures must possess optimal size for regular coverage of the surface. The size of these structures can be as follows: basic dimensions of ~ (5-15) μm; depth ~ (1-3) μm. However, duration of chemical treatment about 70 hours is too long to achieve such large structures.

It was attempted to reduce the time to build these structures by increasing the reaction rate. With this purpose we have gone the way of raising the temperature of the reagent. Different temperatures have been tested, and as the most suitable temperature of 50°C was selected. The composition of etchant was found as 10%KOH:90%H_2O. The duration of the reaction at this temperature was found to be 10-20 min. As an example, the spatial structures obtained by applying the reagent **9** on the Si(100) surface without any preliminary mechanical deformation are presented in Figs. 7, 8.

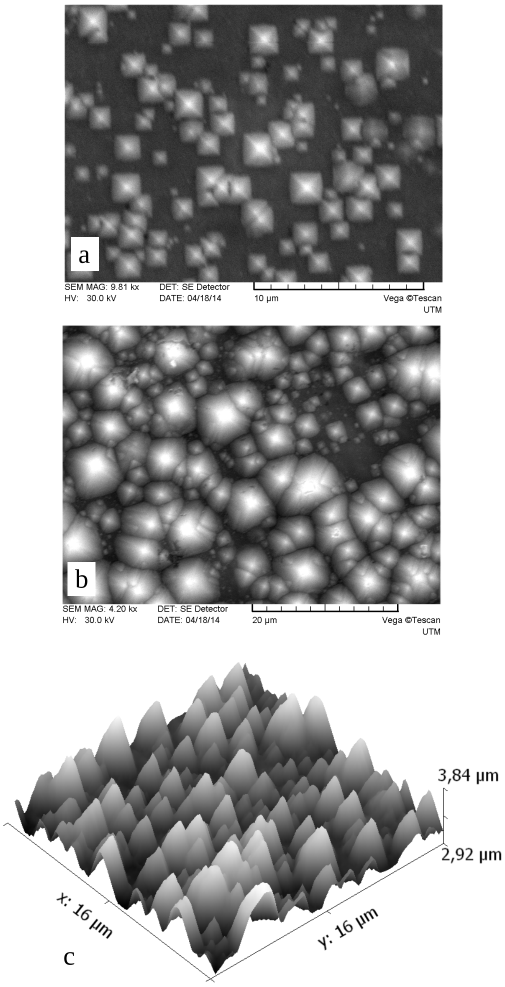

Fig. 7. SEM (a,b), AFM (c). Images of etching pits created on the surface of Si (100) crystal by use the reagent **9** of Tab. 1; *t, min*: a – 10; b, c – 15

Thus, images of structures in Figs. 7 and 8 show us that using reagent **9** Tab. 1 and modeling spatial structures of required shape and density by changing the temperature and reagent concentration can be obtained the structured surfaces on the plane (100) of the Si crystals with purpose of their application in preparation of the solar cells. The proposed method has a great advantage over all of the above discussed methods, because it is characterized by great simplicity and cheapness. It does not require mechanical pretreatment of the silicon surface, as it has the combined properties of the polishing solution, and a selective etchant, forms a uniformly structured surface (see Figs. 7c and 8b) that will efficiently affect the reflectivity of the silicon crystal when used as substrates for solar cells.

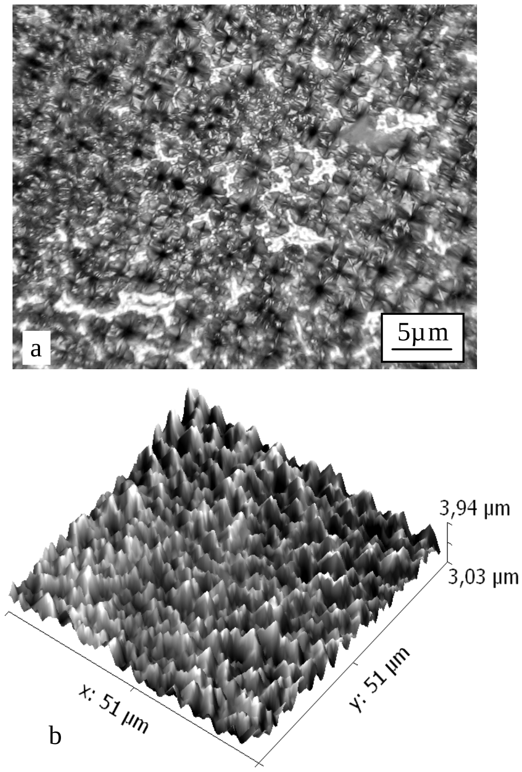

Fig. 8. LM (a), AFM (b). Images of etching pits created on the surface of Si (100) crystal by use the reagent **9** of Tab. 1; *t*=20 *min*

Conclusions

To create the microstructured surfaces of semiconductor materials with subsequent application in solar cells, we put to the test some special mechano-chemical techniques: sclerometric nano and microindentation ('scratching'), "imprinting", blasting, and various tribological regimes in combination with selective chemical treatment. It was found that the 'scratching' in combination with subsequent chemical treatment is the best from all studied mechanical methods and regime of chemical treatment (10%KOH:90%H2O, T=350K, with or without any preliminary mechanical deformation) was found as the most effective for creating the structuring surfaces. The developed in present paper modes of the surface structuring of Si crystals will help to increase the efficiency of solar cells.

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