NANO- AND MICROSCRATCHING AS A POTENTIAL METHOD FOR TEXTURING THE Si SURFACE

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Abstract

The possibility of Si texturing through the use of nano- and microscratching with subsequent chemical etching has been investigated. The influence of the scratching speed, orientation of the indenter (face-on, edge-on) and normal load on the mechanism of deformation during scratching has been analyzed to reveal the favorable loading conditions to obtain plastic scratches. It has been found that the surface of scratches has a corrugated structure that was assumed to be the result of the stick-slip behavior during scratching. Different etching patterns displayed after chemical etching, such as inverse pyramids and a lamellar structure, have been attributed to the specific initial relief of the scratches and etching conditions.

1. Introduction

In spite of a wide range of new materials involved in the elaboration of high-efficiency solar cells, crystalline Si continues to hold the dominant position in PV cell production due to the low-cost technology of fabrication; however, there is a continuous trend for searching for new ways to increase the efficiency of Si-based solar cells. One of the ways is aimed at nano/microstucturing the Si surface [1, 2]. The surface texturing of Si allows reducing the reflection losses and, at the same time, gives rise to the effective area of $p-n$ junction. The efficiency of ITO/SiO_2/Si solar cells was shown to increase by more than 5% only at the expense of texturing the Si surface [3, 4].

Nowadays, different methods are being developed for surface texturing of Si, including laser-structuring [5], mechanical diamond saw cutting [6], electro-chemical etching [7], reactive ion etching [8], and others. The main purpose of all these methods is to provide the possibility of obtaining an optimal geometry and scaling of structural units for the achievement of maximum efficiency and minimum damage induced during processing, for example, by high temperatures (during laser-structuring) or defects (during mechanical texturing and ion etching). An important issue to be taken into account is associated with the duration of the manufacture process and the cost of the final product to be used in large-scale production. The highest efficiency Si solar cells are fabricated by using a defined photolithographic etching mask to obtain a required texture; however, the cost of these cells leaves much to be desired.

In the present work, the possibility of application of nano/microscratching method for texturing the Si surface has been investigated. The scratches were made by moving a diamond indenter and subsequent chemical etching. The main idea lies in the introduction of highly localized stress concentrators into Si surface by means of micro/nanoscratching and the use of these stress concentrators as centers of different chemical activity comparatively with the undeformed volume of the material to obtain a structured surface. In addition, the etching makes it possible to remove the stressed zones and the defects from Si, which is important for the application of silicon in solar cell.

2. Experimental

The scratches were made on a phosphorous-doped Si(100) wafer of a resistivity of 4.5 Ω cm by using a PMT-3NI-02 instrumented nanoindentation installation equipped with a trihedral pyramidal Berkovich indenter and a PMT-3 microhardness tester equipped with a tetrahedral pyramidal Vickers indenter. Scratching was performed by applying a normal force (F_N) to the indenter and by moving it on the sample surface at a constant speed. The scratches were made in the <110> crystallographic direction with both face-on and edge-on of the Berkovich indenter and edge-on of the Vickers one (Fig. 1).

The values of the F_N varied from 2 to 20 mN for the Berkovich indenter and from 5 to 50 mN for the Vickers one. The instrumented nanoindentation device allows adjusting the scratch speed (v), which was set in an interval of 20−400 μm/s; different combinations of F_N and v were used in this study. The scratch speed of about 200−400 μm/s was applied during scratching on the PMT-3 for all F_N used and it was not set automatically. The length of the scratches was up to 400 μm.

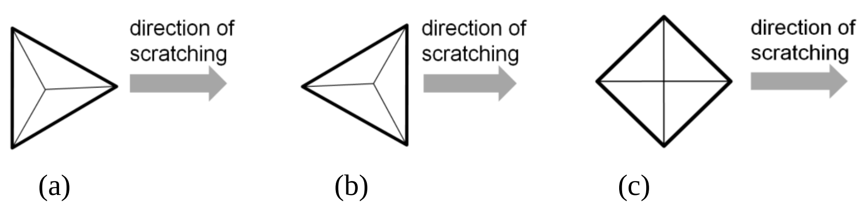

Fig. 1. Scheme of the Berkovich (a, b) and Vickers (c) indenter orientation (showed as the projected contact area) relative to the direction of scratching: edge-on (a, c), face-on (b).

The scratches were subjected to chemical etching in a boiling 30% KOH solution. The morphology and fine relief of the scratches were investigated by atomic force microscopy (AFM, Nanostation II) and light microscopy. Raman spectra measurements were conducted using a Monovista confocal Raman spectrometer with a 532-nm wavelength laser focused on a spot with a radius of about 2 μm in order to study the phase transformation induced by scratching.

3. Results and discussion

The influence of the indenter orientation, scratch speed, and load value on the morphology of scratches is demonstrated in Fig. 2. The scratches made in the edge-on indenter orientation show more pronounced damage compared to those made in the face-on orientation, which is caused by higher stress and strain created under the edge of the indenter than under the face. An increase in load for the same scratch speed (Figs. 2c−2f) leads to the transition from the plastic to brittle deformation mechanism at some critical loads (P_{cr}), which is clearly seen in Fig. 2 by comparing scratches made at 5 (c, d) and 20 mN (e, f). This is also a result of higher stresses created by a higher load.

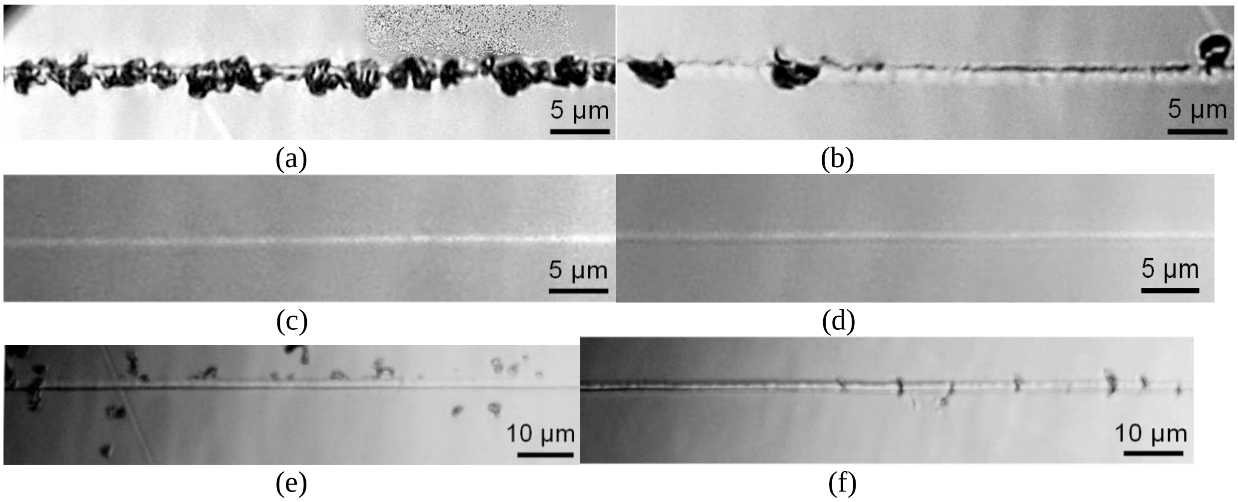

Fig. 2. Light micrographs of the scratches made with the Berkovich indenter at the normal load (F_N) of 5 (a−d) and 20 mN (e, f) in the edge-on (a−e) and face-on (b−f) indenter orientation at a scratch speed (v) of 40 (a, b) and 50 μm/s (c−f).

An increase in the scratch speed for the same load inversely leads to the transition from brittle (Figs. 2a, 2b) to plastic deformation (Figs. 2c, 2d). This tendency indicates that an increase in the scratch speed let the material to withstand higher normal load F_N during scratching without involving the brittle deformation. It was suggested that, with an increase in the scratch speed, the indenter can sleep out from the material [9, 10] and thus diminish the influence of F_N. For 2- and 5-mN scratches made with the Berkovich indenter, beginning with a speed of 50 μm/s, the deformation mechanism is almost plastic for both edge-on and face-on indenter orientation. An increase in the normal load up to 10 and 20 mN requires a higher speed of about 300−400 μm/s for obtaining a plastic scratch track.

The plastic pattern of deformation during the scratching of Si, which is a rather fragile material, is attributed to the phase transition of the initial diamond cubic Si-I structure subjected to high pressure into a ductile metallic Si-II (*β-Sn*) structure underneath the moving indenter. After depressurizing, the unstable phase Si-II transforms into amorphous (*a*-Si) and other crystalline phases (*bc*8, *r*8, *bct*5, *hd*) [11−13].

In our experiments, the measurements of Raman spectra on the scratches made with the Vickers indenter showed the presence only of the amorphous phase in the middle of the scratch groove resulting in a wide peak at 469.44 cm^{-1} [14−16] responsible for *a*-Si (Fig. 3). Towards to the sides of the scratch, where the pile-ups of the plastically displaced material are located, the Si-I with a Raman scattering frequency of 505.84 cm^{-1} was found, which is shifted comparatively with the main peak (522.02 cm^{-1}) obtained from the pristine Si surface. A shift of the main peak is generally caused by tensile or compressive stresses, where the former and the latter lead to a decrease and increase in the Raman frequency, respectively [16]. Thus, a decrease in the Raman frequency of Si-I at the sides of the scratch denotes a tensile stressed structure. This effect may be caused by the presence of dislocations or the interface with the amorphous phase, the presence of which in this zone is confirmed by the shoulder around 470 cm^{-1} (Fig. 3).

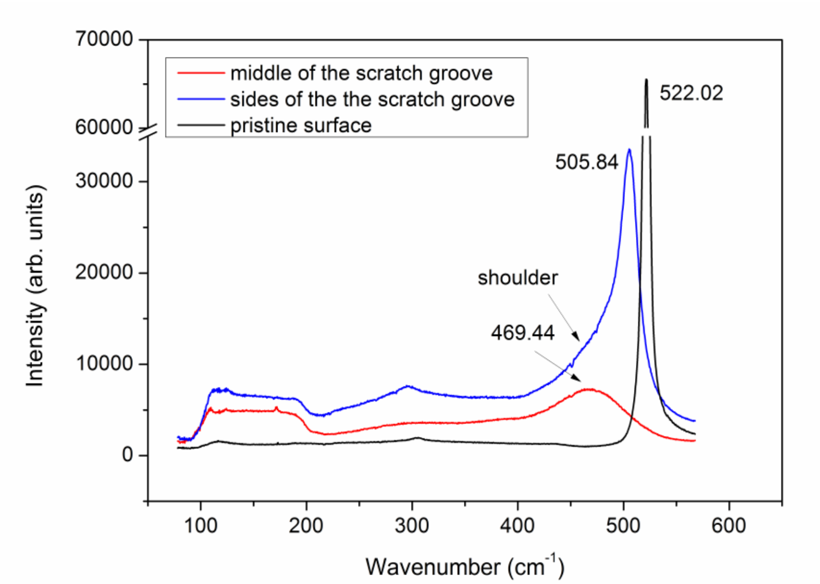

Fig. 3. Micro-Raman spectra of the scratch made with the Vickers indenter, $F_N = 100$ *mN*.

The AFM analysis revealed a fine relief of the scratches, which confirms the above mentioned observations about the influence of the indenter orientation, the load value, and scratching speed on the deformation mechanism. It is evident from Fig. 4 that, for the same load of 2 mN at a scratching speed 20 μm/s, the edge-on scratching exhibits a brittle deformation, by chipping, while the face-on scratching demonstrates a plastic deformation with well pronounced pile-ups of the displaced material at the sides of the scratch groove. In addition, it is clearly seen that the relief of the edge-on made scratch is extremely non-uniform, in contrast with the surface of the face-on made scratch, which shows a more regular structure. Moreover, the face-on made scratch exhibits a corrugated structure, which is also observed on scratches made under higher loads and can be distinguished even in optical micrographs (Figs. 2b, 2f). This feature is most probably associated with the instability of deformation and the stick-slip behavior during scratching [18]. The deformation in nano- and macrovolumes takes place unevenly, by snatching, as a result of an alternation of the accumulation and release of stresses and, accordingly, the slowdown and breakthrough of deformation. During slipping, the material is piled up at the two sides of the scratch groove; at the same time, it also accumulates in front of the indenter braking its moving ahead. To overcome the increased stresses, the lateral force should be increased to a certain critical value after which the breakthrough and the sliding takes place and the stresses drop sharply leading to a decrease in the lateral force. This process is repeated over and over again during scratching and this oscillating wavy deformation results in a waved relief too.

A more pronounced corrugated structure is observed for face-on orientation of the indenter, with a certain combination of F_N and v when the deformation is maintained plastic. With an increase in the scratching speed, the distance between the elements of the waved structure becomes more extended and, therefore, less pronounced. With an increase in the load, the brittle deformation is involved, which leads to the chipping of the material. The use of a Vickers indenter, which induces less stresses due to the larger curvature radius of the tip and the tetrahedral pyramidal shape instead of a trihedral one in the case of a Berkovich indenter [19], gives more plastic scratches for the same F_N and v.

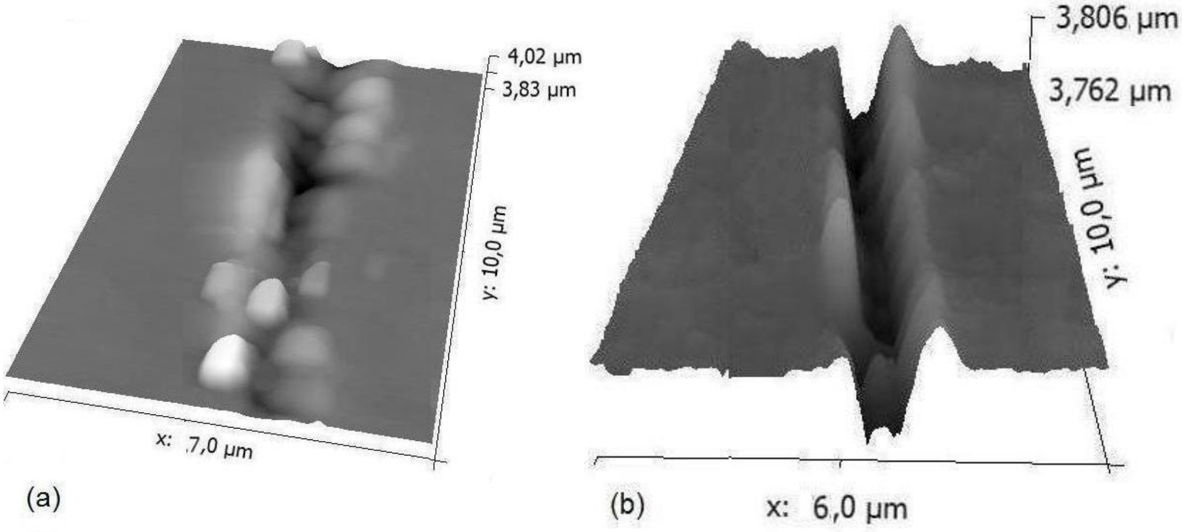

Fig. 4. 3D AFM images of the scratches made with the Berkovich indenter, $F_N = 2\ mN$, $v = 20$ μm/s, edge-on (a) and face-on (b) orientation of the indenter.

The different relief of the scratches induced by different combinations of normal load, scratching speed, type of indenter, and orientation of the indenter gives different patterns after the etching of the scratches. Some of them are shown in Fig. 5. The patterns in Figs. 5a and 5b are formed as a result of the mechanical instability of deformation discussed above and the active {111}<110> crystallographic system for Si (100). The sides of the rectangular elements are parallel to the <110> direction, the same as the direction of scratching. The elements from Fig. 5a are shallow with a large plateau in the middle, unlike those in Fig. 5b representing inverse pyramids, which are more useful for increasing the efficiency of solar cells.

An interesting etching pattern of a lamellar structure shown in Fig. 5c on the array of scratches was most probably created as a result of the instability of deformation alone, as the crystallographic directions are not quite clearly distinguished there. The AFM cross-section profile along the scratch shown in Fig. 5d revealed a serrated structure, which can be effective for solar cells.

Thus, it has been shown that the mechanochemical treatment technique using scratching and subsequent etching can be an efficient method for obtaining a textured surface of Si. By choosing appropriate loading conditions, i.e., normal load, scratching speed, type and orientation of the indenter, as well as appropriate conditions of chemical etching, certain patterns can be obtained. The use of fairly low loads induces minimum damage and stresses into the Si surface; moreover, the subsequent chemical etching removes the stressed and defect zones around the scratch. A larger textured area can be obtained by using a special matrix with an array of indenters instead of a single indenter.

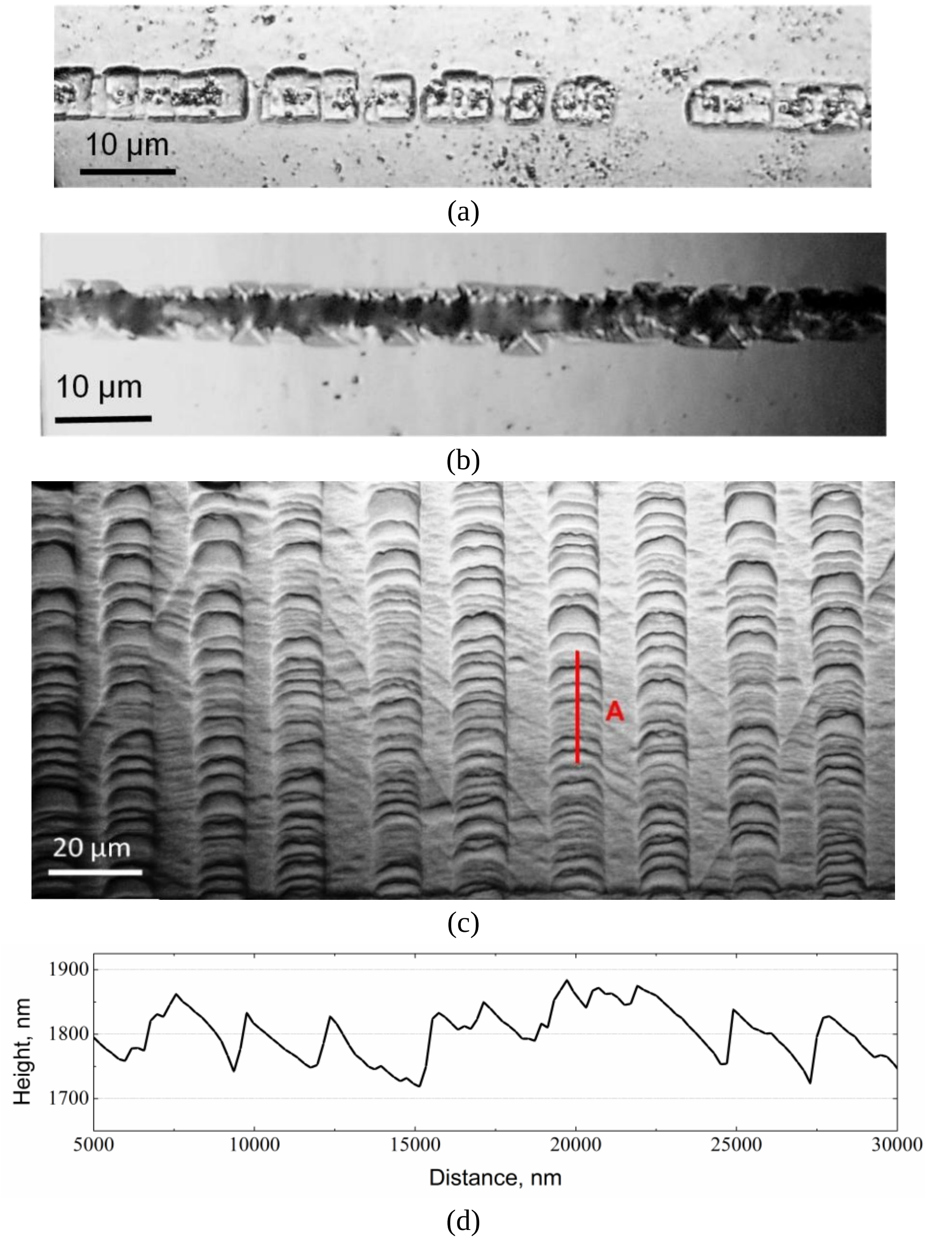

Fig. 5. Etching patterns of the scratches made in the face-on orientation of the Berkovich indenter (a, b) and edge-on orientation of the Vickers one (c) with F_N of 10 (a), 20 (b), and 5 mN (c), and *v* of 50 (a, b) and about 300 µm/s (c). (d) Cross-section profile along the “A” line shown in image (c).

4. Conclusions

It has been shown that nano- and microscratching in combination with chemical etching can be used for texturing the Si surface to be applied in solar cells. It has been found that the scratch speed and the indenter orientation (face-on or edge-on) in combination with normal load value have an effect on the mechanism of deformation during scratching of Si(100). The transition from the brittle to plastic mechanism has been found to occur with increasing scratch speed and decreasing load. In addition, the use of the face-on orientation of the Berkovich indenter provides a more plastic behavior compared to the edge-on orientation under identical loading conditions.

The revealed corrugated relief of the scratches is attributed to the stick-slip behavior during scratching. The chemical etching of the scratches allows obtaining different etching patterns, which depend on the initial relief of the scratch and etching conditions. The inverse pyramids and lamellar structure obtained in this work can be fairly effective textures of Si surface for solar cell application.

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