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Properties of nanocrystalline Si layers embedded in structure of solar cell

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Suppression of spectral reflectance from the surface of solar cell is necessary for achieving a high energy conversion efficiency. We developed a simple method for forming nanocrystalline layers with ultralow reflectance in a broad range of wavelengths. The method is based on metal assisted etching of the silicon surface. In this work, we prepared Si solar cell structures with embedded nanocrystalline layers. The microstructure of embedded layer depends on the etching conditions. We examined the microstructure of the etched layers by a transmission electron microscope and analysed the experimental images by statistical and Fourier methods. The obtained results provide information on the applied treatment operations and can be used to optimize the solar cell forming procedure.

K e y w o r d s: semiconductor, silicon solar cell, microstructure, Fourier analysis

1 Introduction

Suppression of light reflectance from the sample surface is necessary for achieving a high energy conversion efficiency of Si solar cells. Formation of antireflection layers and texturization of Si surface are commonly used for these purposes. The development of new technologies is dominantly motivated by achieving a lower cost of electricity production. Forming of antireflection layers increases the cost of the prepared structures. The spectral reflectance is in this case suitably decreased only in limited ranges of wavelengths and for limited incidence angles. Pyramidal textures formed on Si surface can be used to improve the light trapping [1-6]. The spectral reflectance of a pyramidal texture on Si decreases to 10%. Another way of production of Si structures with a low spectral reflectance is fabrication of porous structures [7-9]. Porous structures are usually nonuniform and due to the thickness of the porous layer it is difficult to form a high-quality pn-junction for the solar cell.

A simple method of forming nanocrystalline layers with ultralow reflectance in a broad range of wavelengths has been developed in Osaka University [10-13]. The method is based on metal assisted etching of Si. A Pt mesh immersed in HF and H_2O_2 solution is in contact with the Si surface and the mesh structure is transferred on the etched surface (surface structure chemical transfer method, SSCT). Due to the nonuniform dissolution, the SSCT treatment forms porous nanocrystalline layers with a gradient of pore density [6]. The ultralow spectral reflectance of nanostructured Si layer/crystalline Si structure results therefore from the depth gradient of the refractive index increasing with the thickness of the SSCT layer. In this work, we prepared solar cell structures with embedded SSCT layers. The microstructure of the solar cells with SSCT layers formed by various technological operations was experimentally measured by the transmission electron microscope (TEM). The cross-sectional TEM image contains important information about the microstructure development during individual steps of forming operations. We analysed the properties of embedded SSCT layers by studying statistical properties of the two-dimensional Fourier transform of a selected area in the TEM image with the SSCT structure. Results of this analysis provide reliable information necessary for optimization of the SSCT forming procedure.

2 Theoretical part

The Fourier transform is an important image processing tool used to decompose an image into its harmonic components. Two-dimensional (2D) image function $f(m,n)$ defined on an $M\times N$ grid selected at the TEM image is in our approach transformed by the 2D discrete Fourier transform [14]

$$F(k,l)=\frac{1}{\sqrt{MN}}\sum_{m=0}^{M-1}\sum_{n=0}^{N-1}f(m,n)\,e^{-2\pi i(\frac{mk}{M}-\frac{nl}{N})}\qquad k=0,1,\dots M-1,\quad l=0,1,\dots N-1 \tag{1}$$

The structure of the Fourier domain $F(k,l)$ is reproduced graphically in a 3D plot (coded into grey scale or in color) and studied by statistical methods. We analysed

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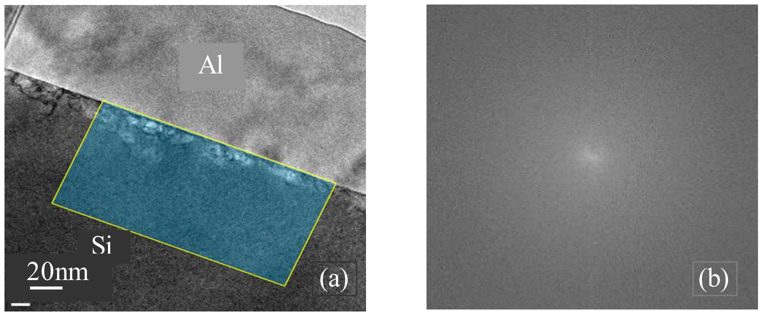

Fig. 1. (a) – TEM image of the Si/SSCT structure with selected area for the microstructure analysis, (b) – 2D DFT map of selected area in the TEM image of the SSCT layer embedded in a solar cell

Table 1. Solar cell structures with embedded SSCT layer

Sample	Etching time (s)
ET05	5
ET10	10
ET15	15
ET20	20
ET25	25
ET30	30

the distribution of the Fourier domain values along selected directions in the $F(k,l)$ space and evaluated the coefficients of skewness and kurtosis. These statistical moments are defined by central moments of the analysed values [15]. The k-th central moment of the random variable X is defined by

$$\mu_k = E(X-\mu)^k, \qquad k = 1,2,\dots \tag{2}$$

where $\mu = E(X)$ is the mean of X. The second central moment μ_2 is called the variance and is a measure of the variability of X values. The coefficient of skewness is defined by equation

$$S_{ku} = \frac{\mu_3}{\mu_2^{3/2}} \tag{3}$$

This is a measure of skewness of distribution X. For positive value of S_{ku} the distribution X has long right tail (distribution is skewed to right). Value

$$S_{ku} = \frac{\mu_4}{\mu_2} \tag{4}$$

is called the coefficient of kurtosis. It is a scale and location invariant measure of the degree of peakedness of the probability density curve. Values of S_{ku} and $F(k,l)$ significantly change in correspondence with the applied solar cell forming operations and indicate the degree of modification of the SSCT microstructure.

3 Experimental part

The SSCT layers in a structure of solar cells have been formed on Si substrate for a set of etching times described in Table 1. Transmission electron micrograph measurements of the cross-section microstructure of the solar cell with embedded SSCT layer were carried out using a JEOL EM-3000F microscope with the incident electron energy of 300 keV.

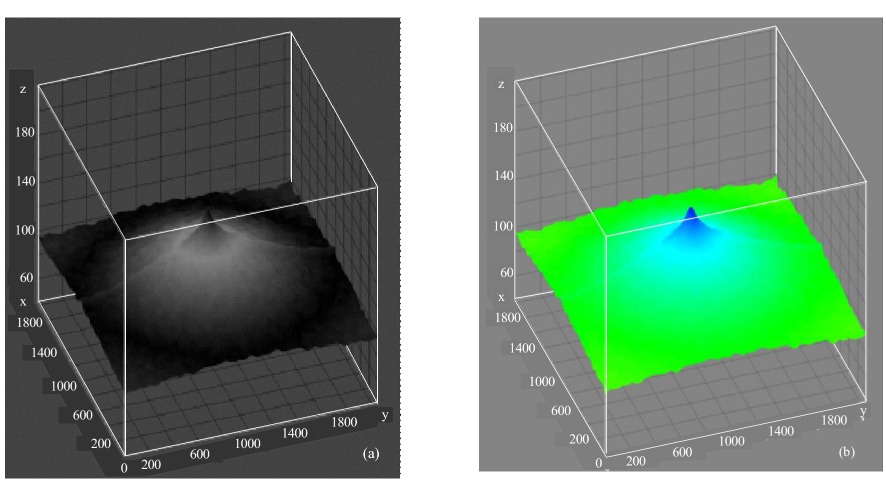

Fig. 2. 2D DFT map of selected area in the TEM image with the SSCT layer : (a) – 2D DFT values represented in the grey scale, and (b) – in the color scale

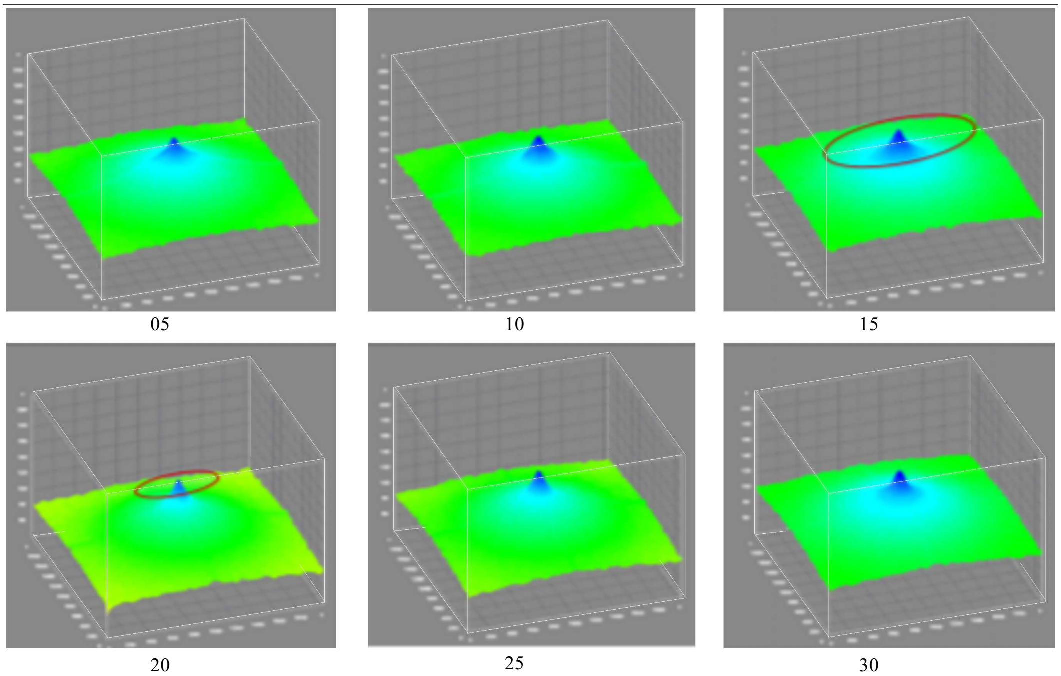

Fig. 3. 2D DFT map of area in the TEM image with the SSCT layer embedded in solar cell, with SSCT layer formed for 5, 10, 15, 20, 25, 30 seconds

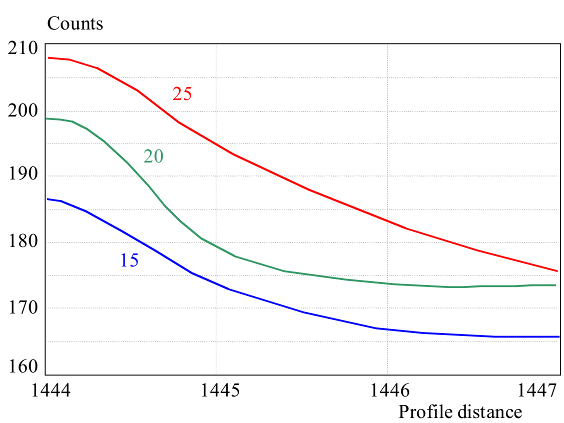

Fig. 4. Detail of the central part of profile shape along diagonal cross - section in the 1st quadrant of the 2D DFT domain, SSCT layer has been formed for 15, 20 and 25 seconds

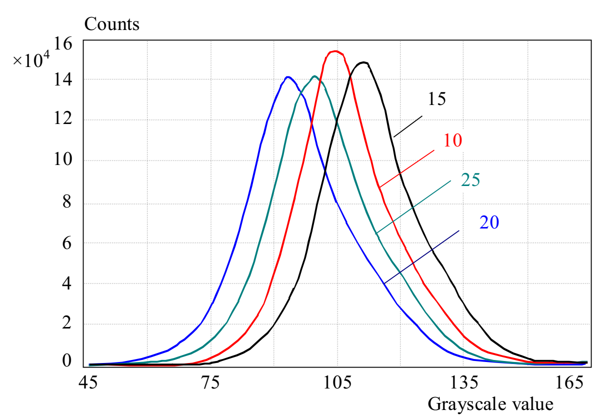

Fig. 5. Histogram of values in the Fourier domain along diagonal cross - section in the 1st quadrant of the 2D DFT domain, with SSCT layer formed for 10 , 15 , 20 and 25 seconds

4 Results and discussion

TEM images of SSCT layers embedded in the structure of the solar cell contain information about the layer thickness and about the microstructural properties influenced by individual steps of technological operations. In the analysed TEM images we selected a rectangular area containing information about the microstructure of the SSCT layer. We used identical dimension of selected areas for the whole set of samples as can be seen in Fig. 1a. The values in the selected area were transformed by the 2D DFT using Eq. 1 and represented in a grayscale 2D image (Fig. 1b), grayscale 3D image (Fig. 2a) and color 3D image (Fig. 2b).

Space frequencies shown in the 2D DFT domain reflect the development of the SSCT microstructure with the prolongation of the etching time. In Fig. 1(b) we observe a bright central zone of the Fourier domain. The properties of this area are very sensitive to changes in the analysed microstructure.

This is nicely documented by Fig. 3 and 4. We observed increasing values and changes of the central peak shape. Significant changes in the central zone can be seen in the ranges between 15, 20 and 25 second of SSCT etching (in Fig. 3 marked by circles). In Fig. 4, the profile values along the diagonal of the 1st quadrant of 2D DFT domain are shown. We observed a significant change of the profile function for etching time 20 seconds again. The distribution of the values for the structure etched for

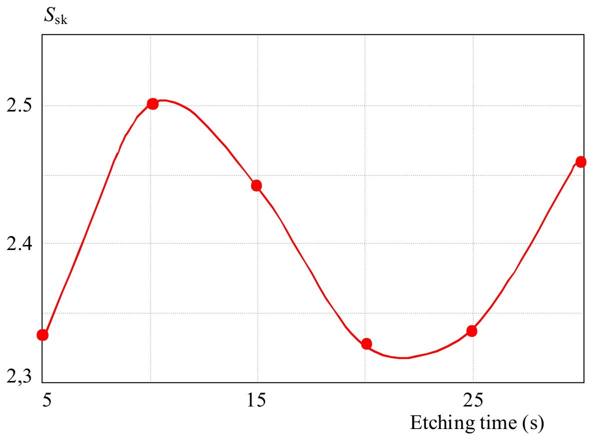

Fig. 6. The coefficient of skewness S_{sk} for distributions represented by histograms in Fig. 5

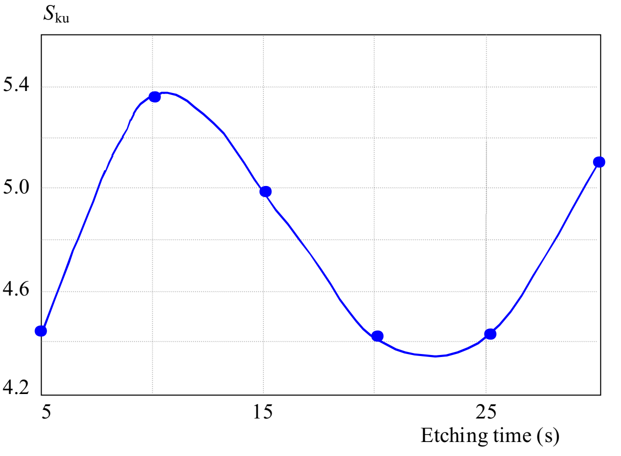

Fig. 7. The coefficient of kurtosis S_{ku} for distributions represented by histograms in Fig. 5

20 seconds is narrower. The properties of particle size distribution in the SSCT layer are different for this etching time.

In Fig. 5, the histograms of values distributed along the diagonal of the 1st quadrant of the 2D DFT domain are shown.. Changes of the histogram shape are determined by changes of particle size distribution in the SSCT layer during etching. In the first steps of the SSCT etching values in the 2D DFT domain represented by histogram shift towards the higher values (up to 15 seconds of etching). This trend drastically changes between 15-20 seconds and relaxes with a further prolongation of etching.

The properties of distributions represented by these histograms are influenced by the development of the SSCT microstructure during etching. Coefficients of skewness S_{sk} and kurtosis S_{ku} computed for these distributions by using (2) and (3) are shown in Fig. 6 and Fig. 7.

The coefficient of skewness increases in the initial stages of etching. With prolongation of the etching time it scales down and reaches minimal values for etching times around 20 seconds. The S_{Sk} values increase after this time again. This behaviour agrees with the development of particle size distribution in the SSCT layers during etching represented by histograms in Fig. 5. S_{sk} values indicate asymmetrical distribution of values in the Fourier domain in comparison with the normal distribution. These values are asymmetric, skewed right and indicate a significant presence of outliers in the right tail of the distribution. This asymmetry increases during etching and reaches less critical values for etching time of 20 seconds. The particle size distribution fabricated during the SSCT etching has lower asymmetry for etching time of 20 seconds in comparison with other SSCT fabricated structures.

Also the coefficient of kurtosis increases in the initial stages of etching. Its behaviour is very similar to the S_{sk} values in Fig. 6. S_{ku} coefficient is a measure of peakedness of analysed distribution. Resulting values of S_{ku} indicate that the distribution in the Fourier domain may be considered as not normal (for normal distribution $S_{ku}=0$). Peakedness decreases for etching time of 20 seconds.

Changes in the SSCT microstructure during the first 20 seconds of etching are substantial for obtaining the required lowering of the spectral reflectance, which is crucial for the solar cell performance. Particle size distribution develops very intensively in the initial stages of etching. During the SSCT etching time of 20 seconds, the formed microstructure features reduce the spectral reflectance in a broad range of wavelengths.

5 Conclusion

Special nanostructured SSCT layers with an ultralow spectral reflectance were formed on a Si surface. The fabricated layers were embedded in the structure of a Si solar cell. The microstructure of nanocrystalline layers formed by various technological operations was experimentally examined by TEM. We analysed the properties of formed SSCT microstructures by 2D DFT transform of selected regions in a cross-sectional TEM image. Distributions of the values in the Fourier domain were analysed by statistical methods. Results of this theoretical approach are consistent, provide reliable information about the intensity of structure modification during the etching procedure and can be used for optimization of the SSCT layer forming steps.

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References

[1] P. Papet, O. Nichiporuk, A. Kaminski, Y. Rozier, J. Kraiem, J.-F. Lelievre, A. Fave, A. Chaumartin and M. Lemiti, "Pyramidal texturing of silicon solar cell with TMAH chemical anisotropic etching", *Solar Energy, Mater.Sol.Cells*, vol. 90, 2006, pp. 2319.

[2] B. Stegemann, J. Kegel, L. Korte and H. Angermann, "Surface Optimization of Random Pyramid Textured Silicon Substrates for Improving Heterojunction Solar Cells", *Solid State Phenomena*, vol. 255, 2016, pp. 338-343.

[3] A. Angermann, J. Rappich, L. Korte, I. Sieber, E. Conrad, M. Schmidt, K. Hübener, J. Polte and J. Hauschild, "Wet-chemical passivation of atomically flat and structured silicon substrates for solar cell application", *Applied Surface Science*, vol. 254, 2008, pp. 3615-3625.

[4] H. Kim, S. Park, S. M. Kim, S. Kim, Y. D. Kim, S. J. Tark and D. Kim, "Influence of surface texturing conditions on crystalline silicon solar cell performance", *Curr. Appl. Phys.* vol. 13, 2013, S34.

[5] S. Jurečka, H. Angermann, H. Kobayashi, M. Takahashi and E. Pinčík, "Multifractal analysis of textured silicon surfaces", *Applied Surface Science*, vol. 301, 2014, pp. 46-50.

[6] S. Jurečka, T. Matsumoto, K. Imamura and H. Kobayashi, "Multifractal analysis and optical properties of nanostructured silicon layers", *Applied Surface Science*, vol. 395, 2017, pp. 150-156.

[7] J. Oh, H. Yuan and H. Branz, "An 18. 2%-efficient black-silicon solar cell achieved through control of carrier recombination nanostructures", *Nat. Nanotechnol.* vol. 7, 2012, pp. 743.

[8] E. S. Kooij and D. Vanmaekelbergh, "Catalysis and pore initiation the anodicdissolution of silicon HF", *J. Electrochem. Soc.* vol. 144, no. 4, 1997, pp. 1296-1301.

[9] K. Tsujino, M. Matsumura and Y. Nishimoto, "Texturization of multicrystalline silicon wafers for solar cells by chemical treatment using metallic catalyst", *Sol. Energy Mater. Sol. Cells*, vol. 90, 2006, pp. 100.

[10] K. Imamura, Jr. F. C. Franco, T. Matsumoto and H. Kobayashi, "Ultralow reflectivity polycrystalline silicon surfaces formed by surface structure chemical transfer method", *Appl. Phys. Lett.* vol. 103, 2013, 013110.

[11] K. Imamura, T. Nonaka, Y. Onitsuka, D. Irishika and H. Kobayashi, "Light trapping of crystalline Si solar cells by use of nanocrystalline Si layer plus pyramidal texture", *Applied Surface Science*, 2016, http://dx.doi.org/10.1016/j.apsusc.2016.04.132.

[12] D. Irishika, K. Imamura and H. Kobayashi, "Sol. Energy Mat. Sol. Cells", vol. 141, 2015, pp. 1-6.

[13] K. Imamura, T. Nonaka, D. Irishika and H. Kobayashi, *ECSD Solid State Lett.* vol. 4, 2015, Q63-Q65.

[14] D. Sundararajan, *The Discrete Fourier Transform, Theory, Algorithms and Applications*, World Scientific Publishing, Singapore, 2001.

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