Coatings of the “Black-Silicon” Type for Silicone Solar Cells

Valerij Yerokhov, Olga Ierokhova

Abstract - **Prospects for preparation of functional “Black Si” multi-layered anti-reflective coating (ARC) of the frontal surface by the electrochemical etching were shown. Both creation of geometrical model of the “Black Si” coating with discreet non-uniformity of a refraction coefficient and technological aspects of the “Black Si” type were described.**

Keywords – **Textures, Antireflective coating, Porous silicone, Solar cell, Electrochemical etching, Photoelectric converter.**

I. Introduction

Anti-reflective coating of the “Black Si” type PEC frontal surface – texturing and formation of similar ARC of frontal surfaces of silicone solar cells is mainly performed to improve their efficiency. Historically, the classic texturing was achieved by the anisotropic etching of mono-crystalline silicon surface to create chaotically distributed pyramids. At the same time, it is possible to create the AR coating of the “Black Si” type by various methods of texturing [1,2,3].

To achieve this goal following methods are employed: femto- and pico-second laser structuring [4,5,6], mechanical cutting by a diamond saw [7], photolithographic etching, optical interference lithography, creation of multi-layered porous silicon by the “dry” and “wet” etching [8], as well as reactive ionic etching (RIE).

To create the “Black Si” type texture we employed the RIE method using the SF6/O2 plasma [9]. Structure of the “Black Si” type texture used for solar cells fabrication is formed by change of the superficial exchange in the RIE plasma with filling SF6/O2.

There is possibility to vary direction of etching from isotropic to anisotropic one because presence of the Cl_2 component in the RIE plasma exhibits with considerably lower etching rates and provides for better control of the texture profile. The “Black Si” texturing is based on the local and regenerating oxide masking. Initially silicon surface is covered with natural oxide, which serves as a masking layer. It is not removed uniformly, but is perforated in the first place.

Non-masked patterns are subjected to etching, and chaotically distributed pyramids with the needle like structure are formed (fig.1).

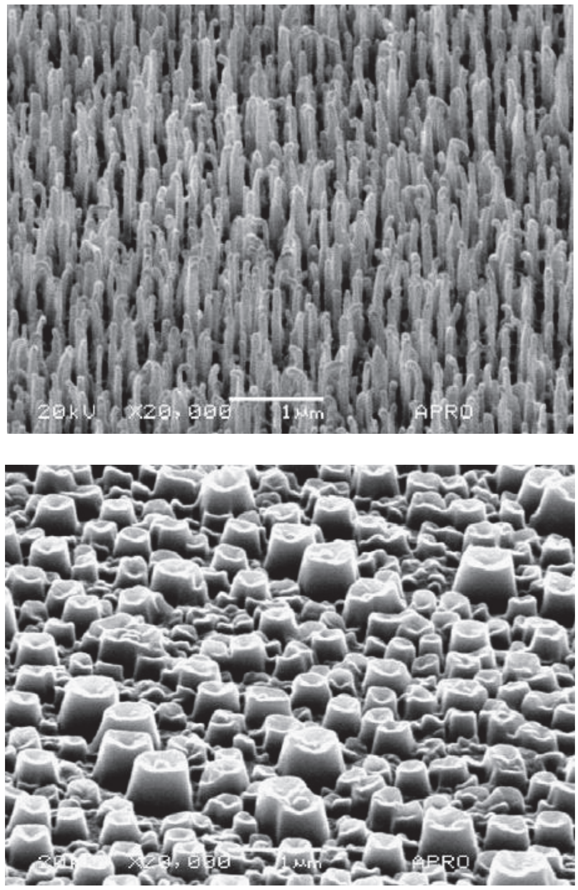


Fig.1 Pictures of the “Black Si” texture taken by the reactive ionic etching in the SEM microscope [9].

In the RIE with SF6/O2 filling they use gaseous SF6 to form the F* radical for silicone etching with formation of gaseous volatile SiF4. Apart from this, the oxygen produces radicals O* for passivation of the lateral surface of silicone by the SixOyFz assisting to control etching profiles. Following the RIE process, liquid chemical superficial destruction-and-removal etching (DRE) is required to diminish degradation of silicon structures. High lifetime of minority carriers is an indicator of low concentration of defects and is important to achieve high efficiency of charge carriers’ absorption.

The goal of this work consists in formation of functional multi-layered ARC of the frontal surface of the “Black Si” type PEC in silicone solar cells by method of electrochemical etching maximally adapted to the processes of silicone SC fabrication.

Valeriy Yerokhov - Lviv Polytechnic National University, S. Bandery Str., 12, Lviv, 79013, UKRAINE, E-mail: v.yerokhov@gmail.com

II. Electrochemical Etching Technology For Multi-layered and Multipored "Black Si" Coating

Majority of textured surfaces reveal satisfactory AR properties only within limited wavelength range (500 … 900 nm), whereas in the near infrared and ultraviolet ranges power of reflected light flux is considerable [10]. For micro-textured surface of silicone formed by femto-second pulse laser radiation, reflectivity does not exceed 10% over wide range of wavelengths (250 … 2500 nm) [5]. Note that such technology requires usage of costly equipment increasing the costs price of the PEC. It is possible to lower the PEC cost by using layers of porous silicone of the "Black Si" type obtained by electrochemical etching [11].

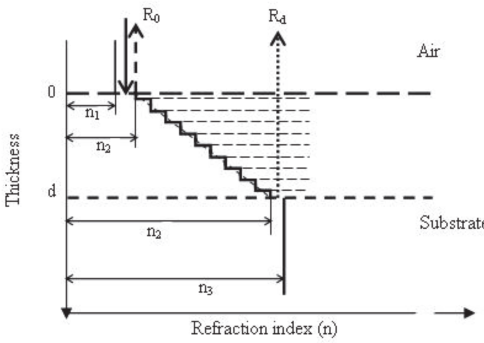


Fig.2 Geometrical model of the "Black Si" coating with discreet non-uniformity of refraction coefficient

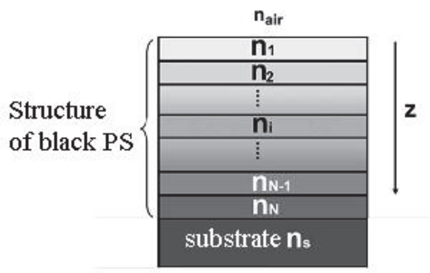


Fig.3 Model of multi-layered and multipored coating of the "Black Si" type.

When using the mono-layer, width of the absorption band is narrow with the V-like absorption curve, and the ARC is not efficient enough. However, to reach the wide-band damping of reflection with the single-layer porous silicone is a complicated task.

It is known that the "thick" layer of porous silicon formed by electrochemical etching can attain 91% of reflectivity reduction in the visible spectral range, but at the same time, it will be just 7% in the near infrared range and approximately the same figure in the ultraviolet spectral range [12].

To attain wide transmission band it is necessary to use multi-layered ARC of interference type, which optical properties are sensitive to optical constants and the coating thickness. The ARC of interference type can be a single layered or multi-layered one. Minimal value of reflection R_{sum} is attained by selection of refraction coefficients and the film thickness of each layer.

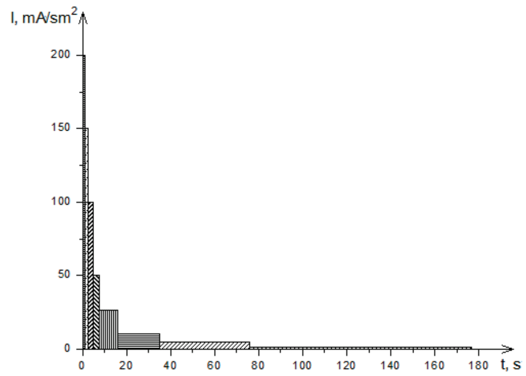
III. Multi-layered and Multipored Coating Creation of the "Black Si" With Discrete Non-Uniformity Coefficient Refraction

Required values of the refraction coefficient for porous silicon can be obtained by selection of electrochemical etching modes. Figure 2 shows geometrical model of the "Black Si" type coating with discreet non-uniformity of refraction coefficient. Number of layers can be arbitrary. Below there are two examples of calculation of the "Black Si" multi-layered and multipored coating up to 10 layers thick based on experimental time diagrams of formation current density (fig.4). It is desirable to have in the ARC not less than 20-30 layers. In this case the refraction coefficient is divided discreetly by the same number (fig.2 and 3) from values of refraction coefficient for air to values of refraction coefficient for silicone.

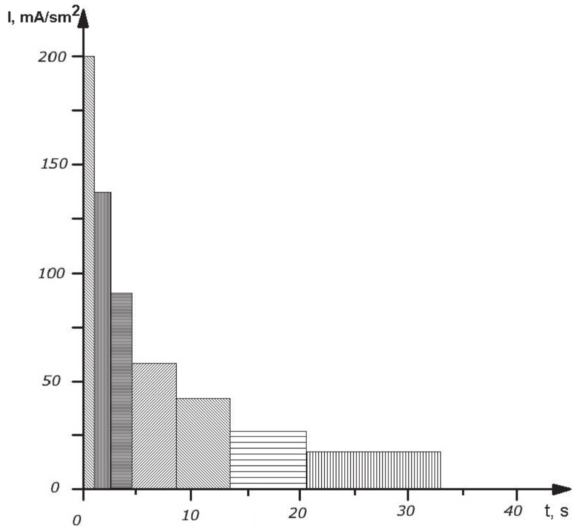
In fig.3, one can see the model of the "Black Si" type multi-layered and multipored coating showing cross-section of a structure with the hopping like variation of refraction coefficients of mono-layers from values of refraction coefficient for air to values of refraction coefficient for silicone, where nair< n1< n2< ····< ni< nN (nair=1, nsi=3,5). Increase in blackening rate in the model depicts growth of the refraction coefficient (decrease of porosity). Thickness of each layer was defined by etching rate, which is a function of time and current density during electrochemical etching. The model thus created and then the multi-layered structure have low reflectivity within broad wavelength range[13].

IV. "Black Si" Technology Fabrication With Multi-layered and Multipored Coating By Electrochemical Etching

To obtain multi-layered and multipored coating on silicone substrate we have proposed method based on the layers formation with ratio of different current density and time, i.e. anodic charge forming corresponding layer. Here, the discreet transition from one mode to another one is critical what was provided for by adequate laboratory equipment (high precision timers, d.c. sources etc.). In this case, relationship between the current density and time satisfies the condition jm·tm=Const, де m, where m – is ordinal number of a monolayer of the multi-layered structure. Current density decreases stepwise from 200 to 10 mA/cm2 according to relationship jm·tm/ jm+1·tm+1=2 та jm·tm/ jm+1·tm+1=1,5 (fig.4a and 4b correspondingl



a)



b)

Fig.4 Timing diagram of the formation current density of the multi-layered and multipored "Black Si" coating formation with ratio of anodic charge of formation of neighboring layers of porous silicon equal to a) 2 and b) 1,5 correspondingly.

V. Study of Experimental Spectral "Black Si" Characteristics With Obtained Multi-layered and Multipored Coatings

Figure 5 shows experimental spectral characteristics of multi-layered and multipored coating of the "Black Si" type for PEC at AM 1,5. From results obtained one can conclude that usage of coating of the "Black Si" type ensures 20 fold decrease of reflection coefficient as compared with the polished surface in the visible spectral range, and 5 fold decrease in the near infrared one. Changes of the reflection coefficient depend on relationship among refraction coefficients and layer lengths. This is caused mainly by interference between light beams reflected from the upper and lower interfaces of the structure created [14, 15].

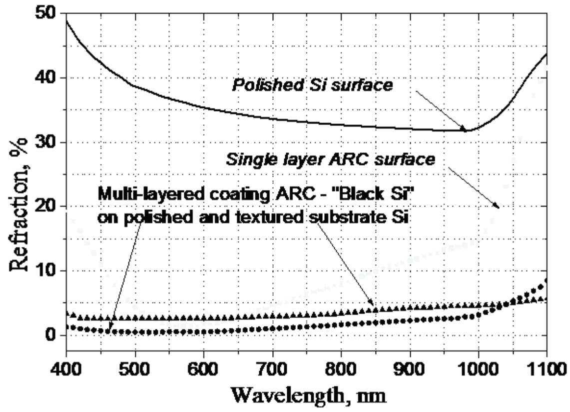


Fig. 5 Spectral reflection characteristics for the "Black Si" coating with discreet non-uniformity of refraction coefficient

Decrease of reflectivity within wide wavelength range can be explained by gradual change of the refraction coefficient over whole structure, in which reflection occurs at each interface between two neighboring layers with different refraction coefficients and reflected beams. Study of the "Black Si" multi-layered and multipored coatings with uncontrolled porosity and discreet variation of refraction coefficient still proceed actively.

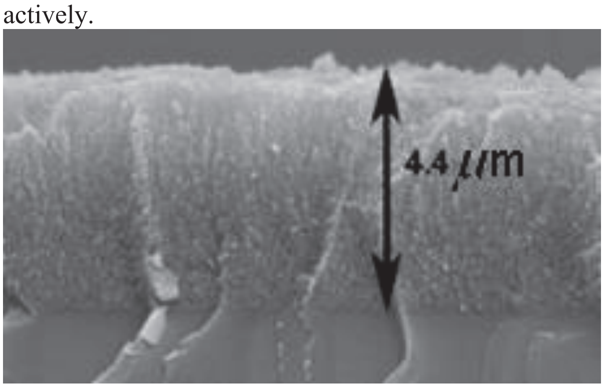


Fig. 6 presents a SEM-picture of transversal chip of the "Black Si" multi-layered and multipored coatings

Figure 6 presents a SEM-picture of transversal chip of the "Black Si" multi-layered structure obtained by the said methods. The sample has porous structure with large pores in its upper part (near border with air) and low-visible small pores in the lower part (near silicon substrate), and their number decreases in the layer depth. Thickness of possible layer of black silicone is 4,4 µm by SEM-measurements.

VI. Conclusion

Principal achievements of present study are as follows:

Development of a model of the multi-layered and multipored coating of the "Black Si" type with discreet non-uniformity of refraction coefficient;

Development of technology of fabrication of the multi-layered and multipored coating of the "Black Si" type by electrochemical etching for textures of the frontal surface of highly efficient silicone SC;

Study of the textures by their spectral characteristics of reflectivity enabling sufficient characterization of frontal surface of highly efficient silicone SC.

New electrochemical technology of porous silicone fabrication based on study of structural features of silicone substrates was developed. The technology comprises stepwise decrease of current density and increase of duration of electrochemical treatment for each individual layer. This allowed to increase both number of layers in the ARC from 2-4 to over 10-20, and the refraction coefficient gradient (typically from values of refraction coefficient for air to values of refraction coefficient for the substrate (1 … 3,4) with discreet non-uniformity in each layer).

Reduction of integral light reflection index to 1% at AM 1,5 within spectral range 400 – 1000 nm has achieved in the result of considerable reduction of the reflection index in the ultraviolet and infrared parts of the spectral range.

Usage of the multi-layered and multipored coating of the “Black Si” type with discreet non-uniformity of refraction coefficient will simplify the technological cycle, and reduce the product cost and improves the SC operating characteristics.

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