Molecular Crystals and Liquid Crystals

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/gmcl20

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https://doi.org/10.1080/15421406.2021.1905280

Formation of the nanoporous Si structure of solar cell with using a model representation

Valerij Yerokhov[a], Anatoly Druzhinin[a], Stepan Nichkalo[a], and Nazar Shtangret[b]

[a]Lviv Polytechnic National University, Lviv, Ukraine; [b]Lviv State University of Life Safety, Lviv, Ukraine

ABSTRACT

In this study, to obtain frontal functional nanolayers of solar cells, an analysis of existing models of PSi was made. In order to achieve a low integral reflection coefficient of a textured Si surface, which can be further used as an efficient anti-reflective coating, a number of experiments were performed to establish the influence of technological conditions on the morphology of porous Si fabricated by electrochemical etching. The results of SEM studies showed that the porous Si surface obtained does not contain noticeable damage or cracking, which indicates the correct choice of technological modes of anodic etching. The obtained porous textures characterized by minimal integral reflection, which is a necessary condition for creating the front surface of Si-based solar cells.

KEYWORDS

Chemical etching; mesopores; nanolayers; nanopores; porous structure; silicon

Introduction

The study of all stages of the formation of porous Si (PSi) structure on the basis of the selected model and identification of patterns that affect the characteristics of the resulting nano-, meso-, macropores are very important. This is because most parameters of porous layers are laid at a stage of the formation of nucleation (or seed) centers. The pore formation mechanism can be described only by a few known models. Among the selected and used by us, which can be used in the creation of solar cell (SC) front surfaces and considered to be the most promising, are Lehmann's model [1] and Zhang's model [2]. In fact, the use of these models contributes to the creation of an efficient and cost-effective nanocoating based on PSi for solar cells [3,4].

To explain the properties of PSi, a number of models that describe the possible mechanisms of pore formation in the PSi layers may be considered. These models can be divided into several groups: a) models describing the quantum confinement of charge carriers in Si crystallites of nanoscale size [5]; b) models describing localized emission caused by Si polysilanes or hydrides formed on the surface of PSi during its growth due to passivation of dangling bonds on the surface [6]; c) models describing the formation of a specific class of Si-O-H compounds (siloxanes) [7]; d) models that combine theories of quantum confinement of carriers and the existence of areas with local defects on

CONTACT Stepan Nichkalo nichkalo@gmail.com Lviv Polytechnic National University, Lviv, Ukraine.

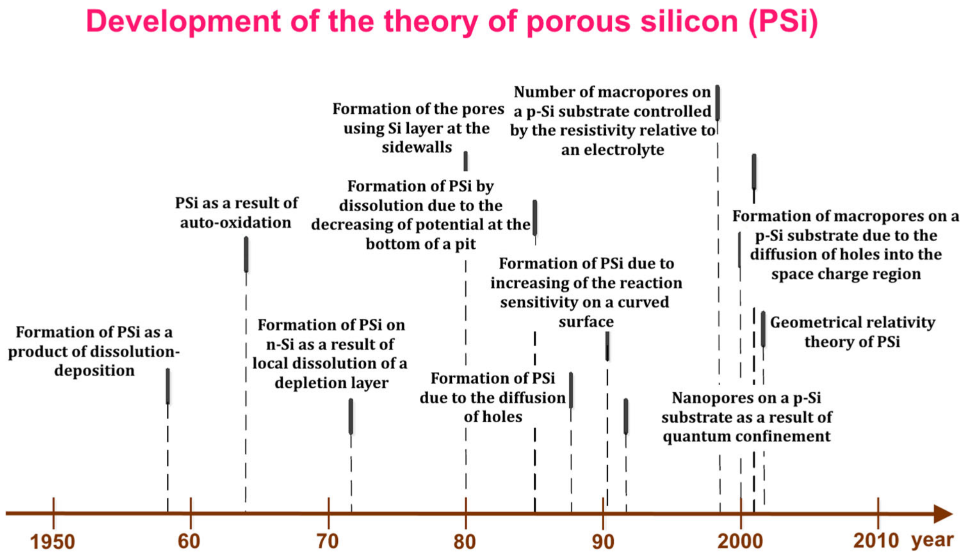


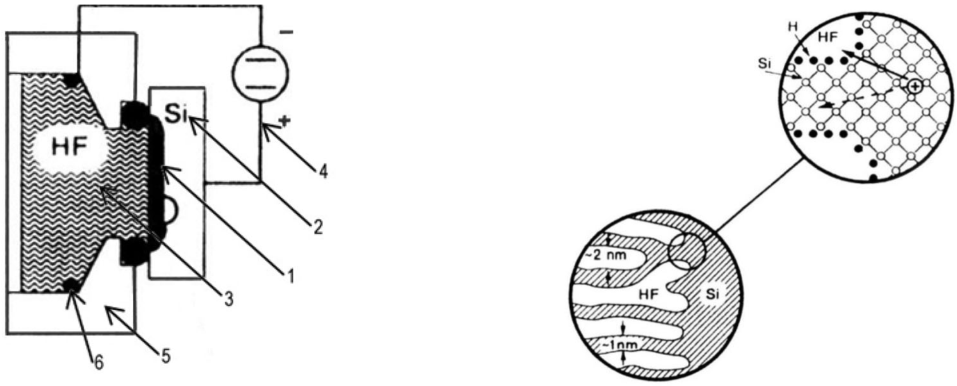
Figure 1. Development of the theory of porous silicon over the past 50 years.

the surface [8], the so-called hybrid models, which better describe the optical properties of the porous film [9–11].

Over the last few decades, many reviews have been found in the literature on the problem of PSi, as well as PSi production technology and the formation mechanism of porous structures. The main milestones in the development of PSi are schematically shown in Figure 1. The latter can provide a huge basis for analysis and future modeling, which we used. Naturally, we classified different reviews using different approaches, such as mathematical, chemical, or physical, later works were classified regarding the dimension of the pores (micropores, mesopores, macropores), and used universal model approaches.

In the early stages of the development of PSi technology, various models of the pore formation mechanism were proposed, in particular, the model of diffusion aggregation [12], as well as models of computer modeling of the porous structure morphology. In these models, it was shown that the final result of anodic etching, which determines the morphology of the porous structure, depends on the characteristic diffusion length, which is a function of the concentration of the doping impurity, voltage, etc. Later, this model was developed by Parkhutik in his work [13]. In particular, it was found that at the bottom of a pore there is a virtual passive film, which prevents direct contact of an electrolyte and a substrate. As a result of a continuous dissolution of Si, a surface layer, and/or a double layer, appears on the Si substrate surface, where pores are formed as a result of increasing the field strength and subsequent dissolution of this layer.

The model [14] takes into account as fully as possible all the processes occurring at the silicon/liquid interface. In this model, it is shown that using current oscillations on the current-voltage characteristics, it is possible to obtain nano-, meso-, and macropores depending on the crystal's orientation. When the local field strength becomes high enough, a local current (current burst) starts to flow. The current flow across the silicon/electrolyte interface is spatially and temporarily inhomogeneous. There are also



a b

Figure 2. (a) – scheme of the production of PSi by the electrochemical etching method (1 – sealant between the HF-based electrolyte and a silicon sample, 2 – Si sample, 3 – HF-based electrolyte, 4 – anodizing line, 5 – teflon case of electrochemical cell-bath, 6 – a part of the counter electrode; (b) – schematical view of the pore's wall and the movement of charge carriers in pores.

other models that combine the phenomena of transport of holes in a semiconductor and ions in an electrolyte, in particular models of linear stability analysis [15–20], a model that takes into account etching reactions [1], a model of local dissolution of Si [21], a model of quantum confinement of charge carriers [22], models of the influence of mechanical stress on the pore formation process [23,24].

Considering and analyzing the methods of forming nanoporous structures on the Si surface for SC, we can identify two basic technologies on which all others are formed, in particular the anode and stain etching. These technologies can be combined to obtain complex nano-multiporous structures [25–27].

Such parameters of nano-PSi layers as porosity and thickness, and for the technological process – growth rate and electrolyte composition, can be considered as basic for the technological process. The most important for the technological process model is the dependence of these parameters on temperature, anode current density, electrolyte concentration, duration of anode treatment, and other conditions of electrochemical etching.

Despite a large number of works, the technological process of pore formation during anodic etching of the Si substrate to obtain the textures of the Si SC front surface needs further investigations. Such known alternative methods of controlling the process of nanopores nucleation on the Si substrate surface as alkaline etching, diffusion doping, ion implantation are more suitable for *n*-type Si, as in the *n*-type a small number of holes is the basis for the electrochemical reaction in a semiconductor.

Therefore, the urgent question is what chemical or physical mechanism accelerates or slows down the Si etching process in different parts of the pore, resulting in a wall between adjacent pores. In this case, how the parameters of anodic etching, the composition of the electrolyte, the properties of Si substrate and its surface can affect the properties of nanoporous Si (diameter of its channel, porosity, the growth direction of individual pores, etc.). It is also necessary to describe the chemical and electrochemical reactions that occur in the Si pore and at the silicon/electrolyte interface. So, the aim of

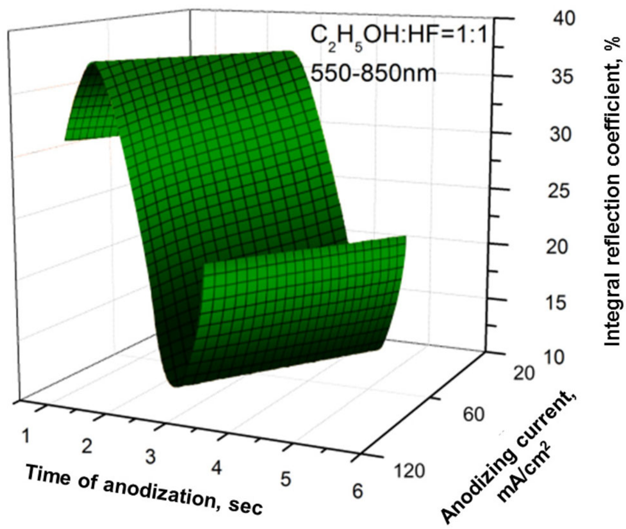


Figure 3. Dependence of integral reflection coefficient on technological conditions of the PSi formation (anode current density and time of electrochemical anodizing).

this work was to develop frontal Si nanolayers by electrochemical and chemical technologies of PSi to obtain efficient and cost-effective technological processes, which can be adapted to the Si SC fabrication process.

Experimental part

Texturing of Si surface by chemical and electrochemical etching is an integral part of the technology of modern high-performance Si SC. The texture on the SC front surface not only reduces reflection losses but also helps to capture long-wavelength light, thereby expanding its operating spectral range and increasing the short-circuit current. Therefore, of particular interest is the study of the effect of nano-PSi layer formation on the anti-reflective properties of a pre-textured Si surface.

Figure 2a shows a schematic of the production of PSi by the electrochemical etching method, where the electrolyte is a mixture of hydrofluoric acid and ethanol ($HF + C_2H_5OH$) in different percentages. Elements of the electrochemical cell-bath are also numbered.

Figure 2b schematically shows the generated model of PSi with nanopores. The pore's wall and the movement of charge carriers in pores are also depicted.

As described above, in the technological process of creating nano-PSi laid models that take into account the etching reactions and local dissolution of Si. All studies we performed in two directions, which included the measuring of experimental parameters and observing in a scanning electron microscope (SEM) changes of the Si surface morphology after the anode etching process. This approach revealed some patterns of the effect of electrochemical anodizing on the anti-reflective properties of the textured surface.

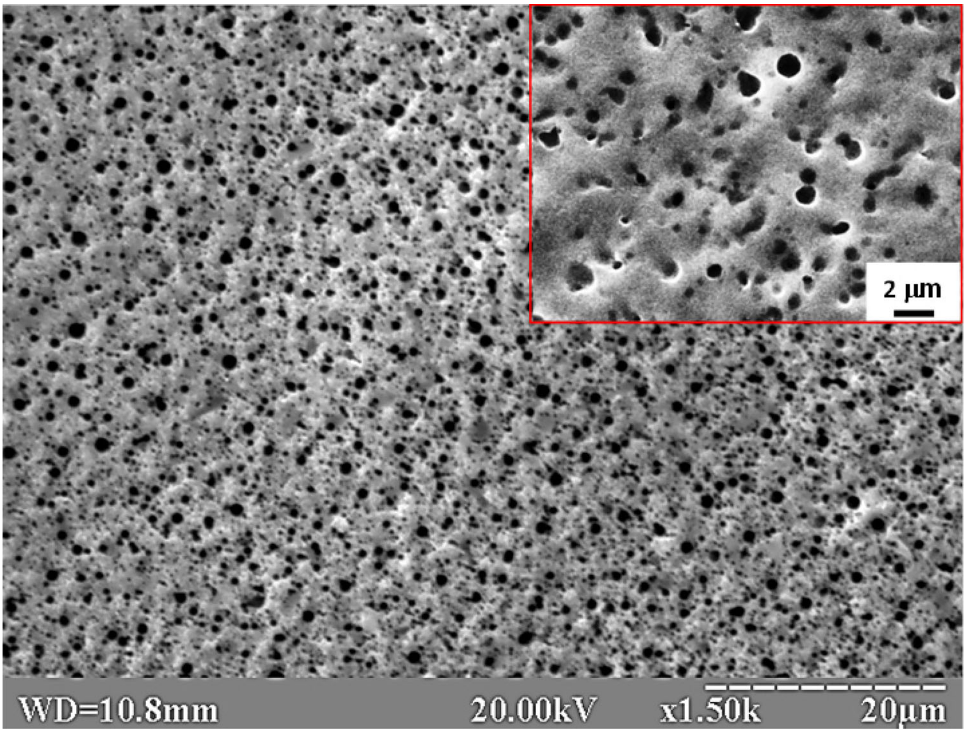


Figure 4. Top-view SEM image of the porous Si surface prepared via electrochemical etching of Si wafer in $HF:C_2H_5OH = 1:1$ (inset depicts an enlarged image of the pores).

Results and discussion

In order to achieve a significant reduction in the integral reflection coefficient of a textured Si surface, which would not be inferior to modern anti-reflective coatings, it is necessary to optimize both the growth process and the parameters of the nanoporous layer to minimize surface texture damage. For this, a number of experiments were performed to establish the effect of anode current, anodizing time, electrolyte composition, and nano-PSi layer thickness on the morphology of Si textured surface and the integral reflection coefficient.

Figure 3 presents the results of the influence of technological conditions of the PSi formation (anode current density and time of electrochemical anodizing) on the integral reflection coefficient of such a structure in the range of 550–850 nm. The anodic etching process was performed in a mixture of $HF:C_2H_5OH = 1:1$.

Since the Si surface is etched in the electrochemical anodizing process, it is obvious that this can lead to partial damage of the base surface texture, as shown in [27]. Violation of the geometry of the base texture, in turn, adversely affects the anti-reflective properties of the textured surface. Thus, the formation of a nano-PSi-based texture layer on a Si surface may not result in the expected reduction in optical losses [17]. However, as it follows from the results of SEM studies (Figure 4), the porous Si surface obtained does not contain noticeable damage or cracking. This indicates the correct choice of technological modes of anodic etching. The average size and distance between the pores can be estimated from the inset in Figure 4. As we can see, the average diameter is less than 1 μm. However, it is difficult to determine the distance between the pores with high accuracy, because the pores are distributed quite chaotically from each other, although quite densely.

In addition, our results showed that in the selected spectral range, the minimum integral reflection is achieved when the thickness of the nano-PSi is in the range from 70 to 100 nm, and the refractive index ranges from 1.35 to 1.9. Satisfactory values of the optical parameters of the PSi layer can be achieved by growing it with the anode current density of 40–100 mA/cm^2 for 2–6 sec. On the other hand, such process conditions make it possible to avoid damage to the surface of PSi texture. The obtained porous textures are characterized by minimal integral reflection (see Figure 3), which is a necessary condition for creating the front surface of Si SC.

Conclusions

The front Si nanolayers made by electrochemical and chemical methods allow obtaining efficient and cost-effective coating for solar cells. The developed models are suitable for creating an efficient and cost-effective coating based on nanoporous silicon, as well as maximally adapted to the solar cell fabrication processes. Satisfactory values of the optical parameters of the PSi layer can be achieved by growing it with the anode current density of 40–100 mA/cm^2 for 2–6 sec. The use of PSi, obtained on the basis of model representation, will simplify the technological cycle, reduce the cost of the product and increase performance, i.e. will increase the efficiency of SC manufacturing technology.

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