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Antireflection and protective films for silicon solar cells

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Abstract. The optical properties of porous silicon structures coated with nanodiamond films have been investigated for use as antireflective and protective coatings of silicon solar cells.

Keywords: silicon solar cells, antireflective and protective coatings, porous silicon structures coated with the nanodiamond films.

1. Introduction

Currently, the most efficient renewable solar energy sources are semiconductor solar cells including silicon solar cells. Silicon is the basic material in the micro- and nanoelectronics, and photovoltaic industry. Because of the high refractive index of a single crystal silicon (n = 3,5), a significant portion of a solar radiation is reflected from the surface of the photovoltaic converter (reflectance value may be greater than 35 %) and, as a consequence, this does not contribute to the carrier pair generation process. Obviously, this leads to an efficiency reduction of these converters. Therefore, the creation of the antireflective coatings and the search for the materials for their production is really important. One of these materials is the porous silicon (por-S), formed on the surface of a monocrystalline silicon (c-Si). Seeing that the porous silicon is degradable, it is reasonable to use the protective films and coatings that do not negate the effectiveness of the solar energy conversion.

The coatings antireflect the light of a visible spectrum are applied on the protective glasses or directly onto the front surface of the solar cells [1-4]. The SiO₂ [1], TiO₂ [2], silicon nitride (SiN_x) [3] and boron nitride (BN_x) films which are good anti-reflective coatings for solar cells because of their spectral stability, high strength and sufficiently wide bandgap [4] are used as the materials with low reflection.

The promising protective materials are diamond-like carbon films (DLC) [5]. DLC effectively absorb the ultraviolet radiation, have a low infrared (IR) absorption, they are transparent to visible light and have the chemical inertness. They not only have the clarifying properties [6-7], but also provide a significant hardening of the functional layers of the porous silicon, significantly increasing the limit of fragility and fracture of toughness at the contact effects [7], and increase the radiation resistance of silicon also [8].

Thus, it should be assumed that the usage of the porous silicon structures with the diamond-like coatings can be one of the methods to increase the efficiency and protection of the silicon solar cells simultaneously.

In this paper we investigate the possibility of creating such structures.

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2. Methods of the experiment

A quite simple technology of electrochemical anodization is used to create the porous silicon. The porous silicon samples was obtained in accordance with a manufacturing route previously developed [9] using the electrochemical anodization technique in the presence of the light sources with the different wavelengths (Fig. 1).



Fig. 1. Electrochemical anodizing device model: 1 – fluoroplastic bath; 2 – anode (silicon sample); 3 – cathode (nickel plate); 4 – electrode holdings; 5 – aqueous solution of a hydrofluoric acid; 6 – light source

Electrochemical treatment of the silicon samples was held in the aqueous solutions of hydrofluoric acid (HF: $H_2O = 1:1$). The cylindrical nickel plate was used as a cathode. The power supply have a range of operating voltages and currents (0.1-100) V and (0.01-5) A respectively was used at the experiment. The silicon substrates – the single crystal silicon wafers KEF-10 (100) before a process of the porous silicon samples producing had being treated in a peroxide- ammonia solution (NH₄OH: H_2O_2 : $H_2O = 1$: 1: 4) at a temperature of 70–90 ° C for 15 min. A nanodiamond (ND) obtained as a result of an explosion synthesis followed by the chemical purification was used as an initial material.

In this research, the nanodiamond films were being obtained from the organic suspensions [10]. The nanodiamond suspensions was prepared as a result of stirring the ND powder in the low-boiling organic solvents (hexane, heptane, octane, toluene, benzene, isopropanol) on application of ultrasound. The transition of the smallest particles in the organic phase occured spontaneously as a result of the simple mixing of the liquids. More intensive transition was initiated by the ultrasonic treatment during which a disintegration of the particles aggregates and a content of the nanocrystalline fractions was increased. The nanodiamond formed the stable transparent suspensions in organic liquids, particularly in toluene, at a solids concentration of 0.01-0.05 g/liter.

The ND film deposition on the silica porous structure was carried out with a dipping method. The presence of the functional groups on the surface of the ND and its high surface energy gives the possibility of the nanoparticles adsorption on a substrate. The optical properties of the ND coatings are controlled by layer thickness and their number depending on the concentration of the suspension.

The investigations of the received samples morphology were carried out with a use of an optical interference microscope MII-4 and the optical properties were investigated with a use of UV-VIS spectrometer Specord M400.

3. The results and their discussion

The research results showed that the electrochemical treatment of the n-type silicon under the additional illumination ($\lambda = 450$ nm) allows to produce the porous silicon layers with high uniformity and the pores equally spaced on a whole surface of the c-Si substrate, as well as a sufficiently high density of the porous structure (Fig. 2). It was found that the blue light ($\lambda = 450$ nm) influences on the simultaneous growth of density and reduction in sizes of the pores (the diameter of the pores is less than 0,5 µm). This contributes to the extension of the porous structures surface area.

The experimental data confirmed the results of this research [11] that showed that the electrochemical anodization technique gives the opportunity to produce structures with the different optical and dielectric properties (refractive index and dielectric coefficient) by varying the programs parameters and conditions of the electrochemical anodization. The increase of current density and temperature of electrolyte results in the increase of pore diameter and change of the optical and dielectric properties.



Fig. 2. Pores diameter dependence on current density and temperature of anodization

Introduction of various structural and technological decisions (change of a cathode form, the pretreatment of Si substrate using supplementary illumination of different intensities and wavelength during the anodizing process, drying of the samples under the influence of the light sources, the exposure time on the air and heat treatment) allows to produce the por-Si films of different thickness, reflectance and refractive indexes and the stability of the optical parameters. In order to obtain thin Si-por film with minimum reflectance (10 %) the following modes of an electrochemical process were determined: the voltage U = 10 V, current density J = 100 mA/cm², the anodization time is 40 min under the influence of wavelength radiation of a visible range $\lambda = 450$ nm.

Morphology, pore dimensions, chemical composition of the porous silicon surface and, as a consequence, the refractive index depends on the shape of the cathode and the lighting of the samples during of their producing. Usage of a cylindrical cathode increases the pores equitability on the plate surface and the reproducibility of the anodization process in comparison with the cathode in the form of a straight plate. In turn, joint use of the cylindrical cathode and additional lighting with $\lambda = 450$ nm allows to produce the thin pores and ordered structure of the porous silicon.

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The results of the spectroscopic studies confirmed that the structures of the porous silicon with ND coatings have the low reflectance (2-8 %) in the visible region of the spectrum compared with the samples of the original single crystal silicon (40-80 %) (Fig. 3a and 3b). The reflection coefficient depends on the number of ND layers (Fig. 3b). The possibility of varying the optical properties due to changes of the number of ND layers and film thickness during suppression allow to form coatings which meet the requirements of the optimal antireflection. The por-Si samples with 10 ND layers have a minimum reflectance coefficient in the range of 600–700 nm, that corresponds to the maximum response characteristics of the silicon solar cell batteries in the area of 600 nm.

The repeated spectroscopic analysis of the samples showed the stability of the optical properties after its expiration for a year.



and por- \hat{S} with the NPD films (b)

According to these researches, the ND films produced as a result of a developed method on the porous silicon does not increase its reflection coefficient. It is shown that depending on the thickness of the ND coating the reflection coefficient changes in the range of 1-4 %,

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which allows to form the coatings which meet the requirements of the optimal reflectance for the solar cells.

In addition, due to their nature nanodiamond coatings have a protective function and stabilize the properties of the porous silicon at the time. It was found that the optical properties of the porous silicon, produced under the optimal conditions, and protected with the nanodiamond coating, did not change during 12 months.

4. Conclusion

The samples of the porous silicon with the equally spaced pores were produced during the process of the electrochemical anodization. It is shown that the porous silicon films effectively reduce the reflection coefficient in comparison with the monocrystalline silicon. The ND coatings were applied on the porous silicon surfaces in order to stabilize the properties and eliminate the degradation processes.

It was established that the ND films produced from the organic slurries practically do not change the reflection coefficient of the porous silicon. It is known that the diamond-like films applied on a working side of the silicon solar cells can increase their resistance to ultraviolet radiation and protons. This point to a perceptiveness of using the porous silicon structures with the nanodiamond coatings as a antireflection and protective coating for the silicon solar cells.

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