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Formation Features of the Porous Silicon Layers Modified by HCl and HBr in the Context of Optical Properties

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Transmission and reflection spectra, refraction factor of the porous silicon layers produced in HF(48%): $HCl:H_2O$ and HF(48%):$HBr:H_2O$ solutions are investigated by the sample illumination and without it. It is established that layers produced by electrolytic anodizing in HF(48%):$HBr:H_2O$ = 16:2:80 mass% solution have the best antireflective characteristics and smaller optical transmission than other samples.

Keywords: Porous silicon, Modification, Photoanodizing, Reflection.

PACS number: 78.20. – e

1. INTRODUCTION

Currently, nanostructured materials are of a great interest. This is connected with their atypical properties in comparison with bulk materials. Porous silicon (PS) which is usually obtained by electrolytic anodizing [1] is one of such materials. At a sufficiently high porosity (≥ 50%) it represents the system of interconnected silicon nanocrystallites whose surface is open for the interaction with other molecules [2]. There are publications where the influence of molecules sorb into pores of PS and which possess acceptor properties on the processes of radiationless recombination is studied. In particular, on the molecules of iodine [3], ammonia [2], nitrogen dioxide, and pyridine [4], Br_2, I_2, KCl, KI [5]. We note that investigation of adsorption of halogen molecules in PS is important for the development of new highly sensitive gas sensors, solar cells, and optical and biomedical applications as well.

On the other hand, properties of PS are sufficiently elucidated in publications [6-12]. Work [7] is devoted to the investigation of PS characteristics. But under the condition of the surface modification, most publications deal with only structural and electrical characteristics of the PS surface [14-16]. Therefore, clarification of the role of modifiers-halogens in the study of the optical properties of the obtained PS layers is considered to be very important.

2. WORK OBJECTIVE

Investigation of the optical properties of PS layers modified by HCl and HBr under the condition of sample illumination and without it is the aim of the present work.

3. BASIC MATERIAL AND INVESTIGATION TECHNIQUE

In the work, we have used plates of monocrystalline silicon KDB-4,5 with (100) orientation of the p-type and the thickness of 300 μm. Concentration of boron dopant was equal to $1 \cdot 10^{16}$ cm^{-3}. Anode etching was performed at room light and sample illumination by incandescent lamp of the power of 500 W. Estimation of the sample porosity was carried out by the gravimetric method. Samples were produced in HF (48%):H_2O:HBr = 16:80:7 – 16:80:2 mass% and HF (48%):H_2O:HCl = 16:80:7 – 16:80:2 mass% solutions during the time from 30 sec to 30 min at the current density of 30 μA/cm^2.

The optical reflection spectra in the spectral range of 190-1100 nm were detected by the single-beam spectrometer "Specord-80". Device uses deuterium and halogen lamps as light sources. The measurement error is equal to ± 20%.

Optical transmission spectra were detected by using the spectrometer SF-46. Diode FD-24K was used as a standard photodetector. On the wavelength λ = 0,9 μm monochromatic sensitivity of the photodiode was equal to 0,57 A/W. The root-mean-square measurement error was ± 5%. Measurements were carried out with the step of 10 nm in the mode of high spectral resolution at the entrance slit size of 0,25 mm. Measurement error of the wavelength λ_i was not more than ± 1% and of the reflection coefficient – not more than ± 5%.

Refraction coefficient was calculated based on the transmission or reflection spectra obtained in the infrared and visible wavelength range [7]. According to this technique, previous values of the refraction coefficients n' were determined

$$n' = 1/(2d\Delta v),$$

where n' is the refraction coefficient; d is the layer thickness; Δv is the difference between wave numbers which correspond to 2 neighbor maximum or minimum ones in the spectrum.

Then we defined the number of interference peak

$$m_{o,e} = [2dn'_{o,e}/\lambda],$$

where $n = m\lambda/2d$ (for maximum); $n = (m + 1/2)\lambda/2d$ (for minimum); m is the order of the interference maximum; λ is the corresponding wavelength.

In order to use PS as an antireflection coating in solar elements, it is necessary to perform the analysis of the optical characteristics of PS layers, such as the transmission and reflection spectra, and the refraction coefficient of PS.

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4. ANALYSIS OF THE OBTAINED RESULTS

Transmission spectra of the PS samples produced in HF:H_2O:HBr and HF:H_2O:HCl electrolytes in the wavelength range of 600-1200 nm are represented in Fig. 1 and Fig. 2, respectively.

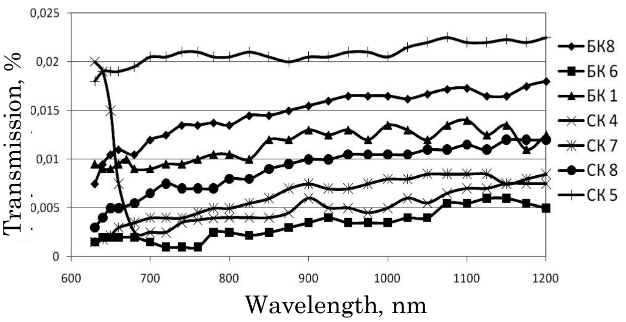

Fig. 1 – Transmission spectra of PS manufactured in solution HF:H_2O:HBr without photoanodizing (СК4, СК7, СК8, СК5) and with photoanodizing (БК8, БК6, БК1)

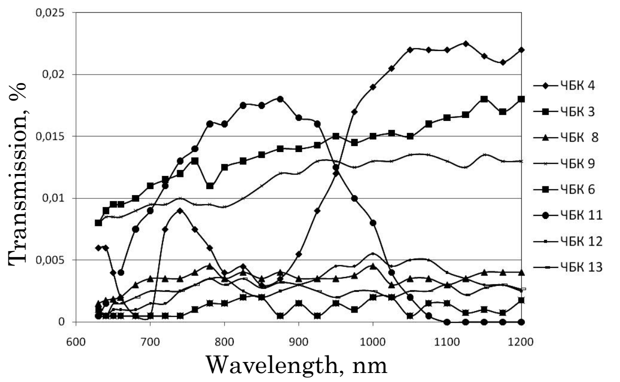

Fig. 2 – Transmission spectra of PS manufactured in solution HF:HCl:H_2O without photoanodizing (ЧБК4, ЧБК3, ЧБК6) and with photoanodizing (ЧБК8, ЧБК9, ЧБК11, ЧБК12, ЧБК13)

It is obtained that the increase in the intensity (see Fig. 1) which is connected with Br molecules located on the surface is observed in the transmission spectra of PS as a result of the increase in the HBr concentration in the solution. As seen from Fig. 1, minimum value of the transmission (0,001%) takes place at the minimum values of HBr concentration which is equal to 2 mass% and at the maximum etching time of 30 min.

The same tendency is observed for the PS samples produced in HF:H_2O:HCl electrolytes (see Fig. 2). At the maximum anodizing time (30 min), intensity of the transmission spectra is the smallest, since the layer thickness of PS is the largest. Increase in the HCl concentration slightly influences the transmission spectra.

Plates with the surface resistance of 400-500 Ohm had stable transmission peaks of 0,018% in the range of 650-1000 nm.

Samples with considerable concentration of defects (10^9 cm^{-3}), which represented the A-type defect clusters [16, 17] and were of spiral form in the cross-section of monocrystalline Si plate, had maximum transmission (0,02%).

In the calculations of the refraction coefficient, the data concerning the dependence of the porosity and the refraction coefficient for PS samples under the condition of photoanodizing and without it (see Fig. 3) is obtained from the transmission spectra. This data indicates that photoanodizing significantly influences the change in the PS properties. Refraction coefficient and porosity of the samples produced in HF:HCl:H_2O solution with photoanodizing is changed from 0,8 to 3,3 and 40-82%, respectively; from 0,83 to 2,75 and within 42-86% – for the samples manufactured in HF:HBr:H_2O solution; without photoanodizing – from 0,5 to 1,5 and within 32-66% for the samples produced in HF:HCl:H_2O solution; from 0,7 to 0,98 and within 67-80% for the samples manufactured in HF:HBr:H_2O solution.

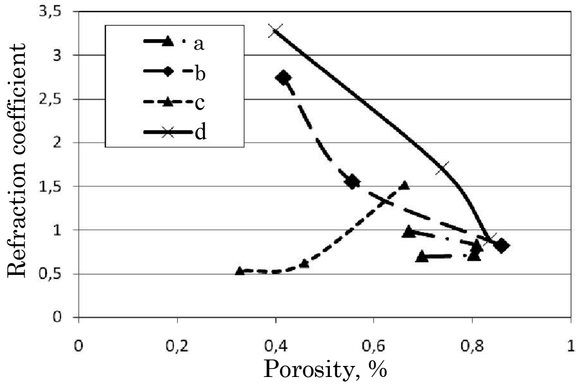

Fig. 3 – Dependence of the refraction coefficient on the porosity: for samples produced in HF:HBr:H_2O solution without photoanodizing (a); at photoanodizing (b); for samples manufactured in HF:HCl:H_2O solution without photoanodizing (c), at photoanodizing (d)

Analysis of the samples in anodizing time gives the following distribution in the refraction coefficient and porosity (Fig. 4). Refraction coefficient within 3,3-1,7 is typical for samples produced during 1 minute; within 1,5-0,8 – for samples manufactured during 10 minutes; 0,7-0,55 – for samples anodized during 30 minutes.

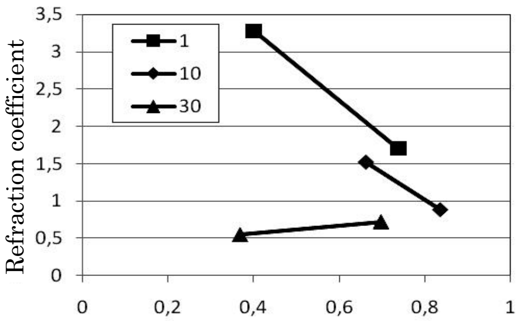

Fig. 4 – Dependence of the refraction coefficient on the porosity of the sample produced in HF:HCl:C_2H_5OH:H_2O solution at photoanodizing (the names of the dependences are the times of sample anodizing, amount of minutes)

Experimental optical reflection spectra for a ground surface of monocrystalline silicon (a), for samples produced in solutions HF(48%):C_2H_5OH:H_2O = 16:4:80 (f), HF(48%):HCl:H_2O = 16:7:80 (c), HF(48%):HCl:H_2O = 16:2:80 (d), HF(48%):HBr:H_2O = 16:2:80 (e), HF(48%):HBr:H_2O = 16:7:80 (b) are represented in Fig. 5.

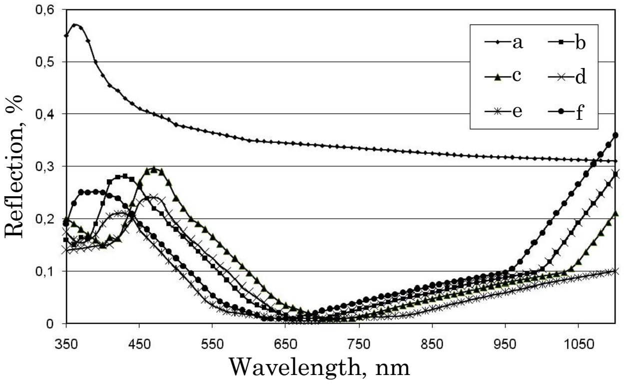

Fig. 5 – Reflection spectra for the ground surface of monocrystalline silicon (a); for the samples manufactured in solutions HF(48%):C_2H_5OH:H_2O = 1,6:0,4:8,0 mass% (f), HF(48%):HCl:H_2O = 1,6:0,7:8,0 mass% (c), HF(48%):HCl:H_2O = 1,6:0,2:8,0 mass% (d), HF(48%):HBr:H_2O = 1,6:0,2:8,0 mass% (e), HF(48%):HBr:H_2O = 1,6:0,7:8,0 mass% (b)

The best results in the whole investigation area of antireflection losses were shown by samples produced in HF(48%):HBr:H_2O = 16:2:80 mass% solution. Here we have to note that in the range of $\lambda \sim 650$ nm, minimum reflection losses are observed.

It is known [11] that PS during the contact with air can considerably change own properties. Therefore, for the effective practical application as an antireflection coating of solar element, it is necessary to study the stability of the reflection characteristics of PS surface during the aging process. In Fig. 6 we illustrate the reflection spectra of PS in one day after its formation and after six months on air.

As seen from Fig. 6, for the sample characteristics in six months one can notice the same behavior of the reflection coefficient spectral dependence. Deterioration of the reflection characteristics (~ 15%) of PS layers is observed.

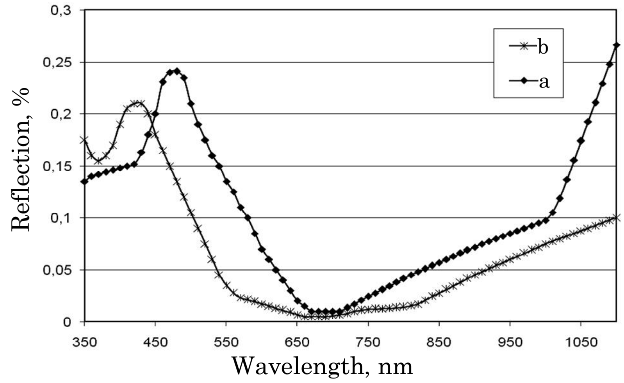

Fig. 6 – Changes in the antireflection characteristics during aging in air: sample in one day after production (b); sample in six months (a)

5. CONCLUSIONS

In the present work, it is established that PS layers produced in HF(48%):HBr:H_2O = 16:2:80 mass% solution had the lowest antireflection and transmission characteristics.

Analysis of the samples with respect to the anodizing time shows layering in areas in the refraction coefficient. The first area of the refraction coefficient within 3,3-1,7 is typical for the samples produced during 1 minute; the second area within 1,5-0,8 – for the samples manufactured during 10 minutes; the third area (0,7-0,55) – for the samples anodized during 30 minutes.

Deterioration of the reflection characteristics (~ 15%) is observed during the sample aging.

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