Investigation of Influence of Electronic Irradiation on Photoluminescence Spectra and IR-spectra of Porous Silicon

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Abstract - Investigation of the influence of electron irradiation on PS photoluminescence (PL) spectrum and PS IR-spectra is presented in the this paper. Both newly-prepared PS samples and samples prepared a year ago were subjected to irradiation. It was shown that the shape of PL spectra and the half-width of the curve did not change for both types of samples. In case of electron irradiation in air, photoluminescence of newly-prepared PS samples showed the highest rate of degradation, which depended on the PS film thickness: the thinner the PS film, the stronger the degradation. When the dose rate was more than 10¹⁵ cm⁻², the intensity of PL spectra decreased, and when D was equal to $10^{16} \ \text{cm}^{-2}$ the intensity decreased by a factor of 4. It was discovered that among the thick PS layers, the long-stored samples, which practically had no oxygen, possessed the best radiation resistant properties. Oxygen passivation causes increase in PS radiation resistance and for $D = 10^{16} \text{ cm}^{-2}$ it only decreases by 20%.

1. Introduction

The influence of radiation on structural and luminescent properties of porous silicon (PS) has been extensively studied recently [1, 2]. For example, in [1] the authors studied the influence of 2-MeV electrons irradiation at dose rates of $10^{16}-10^{17}~\rm cm^{-2}$ on the conductivity and PS resistivity, and they mentioned possibility of generation of such defects into silicon monocrystals. In [2] PS was subjected to 20-Kev electrons irradiation and the irradiation results showed increase in the number of oxygen groups and decrease in the number of hydrogen groups.

The aim of this paper is to study influence of 2-Mev electron irradiation on PS composition and its luminescent properties.

2. Experimental technique

The authors studied the PS layers formed on the surface of p-type monocrystal silicon wafers with resistivity of 10 Ohm/cm, orientation (100) and polished from both sides. In order to form a PS layer we used a process of electrochemical anodizing in modified electrolyte in the mixture HF: and oxidized alcohol in ratio 1:1.5. The electrolyte used in this work enables to obtain a photoluminescent PS at low current density about 0.1 mA/cm², moreover, in this case the PS layer

is uniform. The films used for irradiation were formed by current density 20 mA/cm² and anodizing time varying from 10 s to 30 min. Maximal thickness of porous silicon layer was about 20 um.

Electron irradiation was carried out at room temperature by linear accelerator "Electronik ELU-4"; the energy of electrons was 2 MeM, current density was 1 μ A/cm², irradiation doses were 10^{14} , 10^{15} and 10^{16} electrons/cm². The PS samples temperature during irradiation did not exceed 30 C. Samples were wrapped into aluminum foil during irradiation. For irradiation we used not only newly-prepared PS samples but also samples made a year ago.

Photoluminescence was measured at room temperature at KSVU-23 device using as a radiation source impulse laser ILGI-503 operating on molecular nitrogen in a quasi-continuous mode at wavelength 337 nm. The porous silicon composition was determined from infrared absorption spectra measured in the range 400 – 4000 cm⁻¹ by Perkin-Elmer Fourier spectrometer FTIR-1700.

In this research the influence of radiation was studied using two types of specimens: newly prepared specimens and specimens after their long storage in the air environment. It was done because PS may interact with oxygen during its storage in the open air [4, 5], which causes gradual replacement of Si-H bonds by Si-O bonds on the surface of silicon nanocrystal. This process is accompanied by luminescence reduction at early stages and by restoration and stabilization of luminescent properties after long storage.

3. Photoluminescence spectrum

Let us first consider the spectra of newly-prepared PS samples formed during different anodizing periods (from 10 s to 25 min) giving different values of PS thickness and porosity. PS photoluminescence spectra before irradiation are shown in Fig. 1.

As the PS layer thickness increases the intensity of photoluminescence also increases with slight (about 5 nm) peak shifting to the short-range part of the spectrum. The size of nanocrystals of newly prepared samples calculated by the method of singling out of spectrum components [10, 11] was equal to 3.8 nm.

After a dose rate of 10¹⁵ cm⁻² irradiation the spectrum maximum position practically did not change. The intensity of PL peak for samples formed for ano-

dizing periods of 10 s, 30 s, 2 min and 25 min decreases by 30%, 20%, 10% and 5%, respectively, as compared with the curves obtained before irradiation. It means that the decrease in PL spectra intensity increases with the decrease in the PS layer thickness. It evidences the action of a secondary surface-active factor accompanying the irradiation process. Air exposure causes quick restoration of PL intensity of irradiated PS samples.

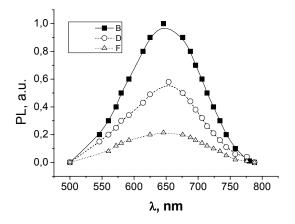


Fig. 1. PS photoluminescence spectra before irradiation for thin PS samples formed during the following time periods: 1 - 10 s, 2 - 30 s, 3 - 25 min

After Irradiation with a dose rate exceeding 10¹⁵ cm⁻² causes considerable reduction in the intensity of PL spectra of newly-prepared PS samples (Fig. 2). The position of maximum in PL spectrum practically does not change.

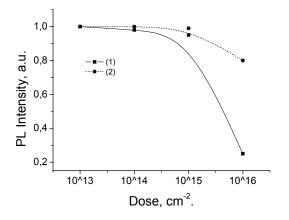


Fig. 2. Influence of the dose rate on the intensity of PL spectra of a newly-prepared PS sample (1) and after their long storage.

There is no hydrogen in the PS samples stored for a long period of time. Maximum of PL intensity for long-stored samples corresponds to the wavelength 660 nm. Shifting of the maximum to the long-wave region after long-term storage is probably caused by oxidation of large-size crystallites, which leads to the decrease in silicon "core" and their involvement in the PL. Long-stored porous silicon turned out to have the best radiation resistant properties. The intensity of PL spectra of long-stored PS samples after their a dose 10^{16} cm⁻² irradiation only decreased by 20%.

4. IR transmission spectra of porous silicon

Changes in PS composition during irradiation may be studied comparing absorption IR-spectra before and after irradiation. Fig. 3 shows IR-spectra of different thickness PS samples before irradiation formed during the time period from 10 s to 25 min. In 10-s anodizing (3a) case only two peaks of oxygen absorption at 1100 cm⁻¹ (Si-O-Si) – an extension mode and hydrogen absorption at 620 cm⁻¹ (Si-O) – a deformed mode are observed. For 30s treatment an additional peak 860 cm⁻¹ (Si-O) appears, this peak also corresponds to the deformation mode. In case of 2-min and 25-min anodizing the above absorption lines become more intensive.

IR-spectra of newly-prepared PS samples are shown on the right side of Fig. 3. Thin PS samples do not reveal clearly pronounced absorption bands in all wavelength range except the line 2300 cm⁻¹ which may be caused by the oxide film of SiO₂ on silicon.

In PS samples whose formation time exceeded 2 min, both oxygen and hydrogen absorption bands were enhanced. PL spectra of such samples only weakened by 5-10~%.

IR-spectra of long-stored (before irradiation) samples all absorption lines caused by hydrogen are absent. In this case we observed absorption for wavelengths 1100, 860 and 460 cm⁻¹, caused by oxygen bond by silicon and lines 2800-2900 cm⁻¹ showing carbon presence. In the vicinity of 2250 cm⁻¹ there are vibration modes of 0₃-Si-H bonds.

If irradiation doses do not exceed 10¹⁶ cm⁻² all absorption lines present before irradiation remain, and in addition a thin line of 730 cm⁻¹ corresponding to Si-C bond appears.

5. Conclusion

In case of electron irradiation in the air environment, the highest rate of degradation was observed for photoluminescence of newly-prepared PS specimens. When the dose exceeded 10¹⁵ cm⁻², a sharp reduction in PL spectra intensity was observed, which depended on the PS film thickness: the thinner the PS film, the stronger the degradation.

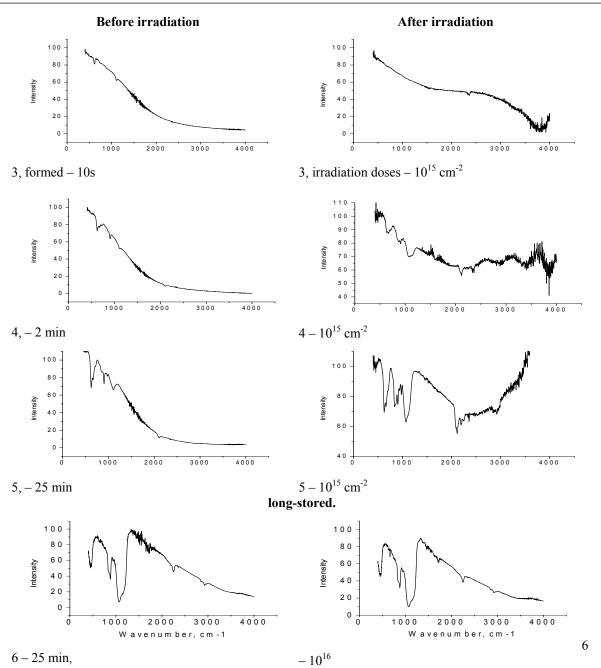


Fig. 7. IR absorption spectra of PS samples formed during the period ranging from 10 s to 25 min before and after irradiation

When the dose rate was equal to 10¹⁶ cm⁻², the PL spectra intensity decreased by a factor of 4. It should be noted that a considerable influence of ozone formed in air during irradiation may be observed.

Long-stored specimen, which practically had no oxygen, turned out to have the best radiation resistant properties. Oxygen passivation causes increase

of PSradiation resistance. The electron dose rate of $D = 10^{16}$ cm⁻² decreases PL intensity by 20%.

Refferences

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