Photoluminescent properties of porous silicon samples with electrochemically deposited 3d-metals

Maarif A. Jafarov, Huseyn M. Mammadov, Vusal U. Mammadov[*], Elshan F. Nasirov

Baku State University, Baku, Azerbaijan

Abstract

A technique has been developed for obtaining 3d-metal/por-Si at electrochemical deposition and co-deposition of iron and cobalt into a porous silicon matrix Based on the results of the experiment, it can be concluded that the chemical deposition of various metals of the iron group has a similar effect on the composition of the porous layer. With the joint deposition of iron and cobalt in porous silicon of the n type, cobalt promotes a deeper penetration of iron into the porous layer. The influence of the deposited metal on the position of the peak of the photoluminescence intensity of 3d-metal/por-Si nanomaterials is shown.

1. Introduction

The study of samples of meso- and macroporous silicon showed a good correspondence between the characteristics of these materials for the purposes of solar energy, provided that it is possible to eliminate the harmful effects associated

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* V.U.Mammadov. Tel.: +994506646384
E-mail address: vusalmammadov@bsu.edu.az

with the presence of thermal and photosensitive bonds on the surface of nanomaterials using standard technological methods [1-3]. Macroporous silicon, in general, in terms of its composition and response to exposure to solar radiation simulator in a mode close to that of solar element, much closer to crystalline silicon than mesoporous. At the same time, the presence of PL, although relatively low, with a maximum in the region of 600–700 nm in macroporous silicon may indicate the presence of a certain amount of silicon nanocrystals in its surface layer [4,5]. In this case, we believe that the same decrease in the PL intensity of macroporous silicon on the side of the sample exposed to the solar radiation simulator and on the opposite, dark side of the sample can be caused by desorption under the influence of temperature of the bonds adsorbed on the surface with the formation of nonradiative recombination centers with the overall composition and sample structures. Mesoporous silicon in its composition differs more strongly from crystalline silicon than macroporous silicon and has a more developed surface, saturated with various types of bonds and in the process of exposing the sample to the imitator of solar radiation, small structural changes are observed [6-8].

2. Experimental

The formation of porous silicon samples with galvanically deposited metals of the iron group, as in the case of chemical deposition, took place in two stages:porous matrix and precipitation of metal from a solution of the corresponding salt. Plates were used as the starting material for the formation of the porous layer single-crystal silicon grade (silicon doped with phosphorus) with resistivity ρ = 0.2 Ω/cm^2 and orientation (100). Electrochemical etching of wafers with S(100)i was carried out in a galvanostatic mode at a current density of ~15 mA/cm^2 for 10 minutes in a 40% HF solution in isopropyl alcohol with the addition of a 10% hydrogen peroxide solution in the ratio [2:2:1] (standard technique). Immediately after etching, porous silicon samples were washed in distilled water and then in isopropyl alcohol to remove electrolyte residues from the pores.

Before electrochemical deposition, the samples were immersed for 20 minutes in a salt solution of the corresponding metal to ensure good penetration of this electrolyte deep into the pores The deposition of Fe, Ni and Co into the porous layer was also carried out in the galvanostatic mode. In this case, the polarity of the power source changed to the opposite, i.e. the silicon wafer served as the cathode. The current density during deposition was 0.5 mA/cm^2, deposition time ~ 60 minutes. Precipitation was carried out from an aqueous solution of iron sulfate ($Fe_2SO_4 \cdot 7H_2O$), nickel ($Ni_2SO_4 \cdot 7H_2O$), or cobalt ($CoSO_4 \cdot 7H_2O$) with a concentration of 0.1 mol/l. The pH of the solution was maintained at ~ 3 by adding

sulfuric acid precipitation to the solution. After deposition, the samples of porous silicon were washed in isopropyl alcohol for 10 seconds and dried in the atmosphere. Co-precipitation of Co, Ni and Fe was also carried out at various ratios of the volumes of the corresponding solutions (3:7, 5:5 and 7:3). Electrochemical etching and deposition were carried out in low light conditions at room temperature. All the obtained samples exhibited sufficiently bright visible photoluminescence in the red region of the spectrum when they were irradiated with an LGI-21 pulsed gas laser with a wavelength of $\lambda = 337$ nm.

Before etching, SEM images of the surface of the samples were obtained (Figure 1a)
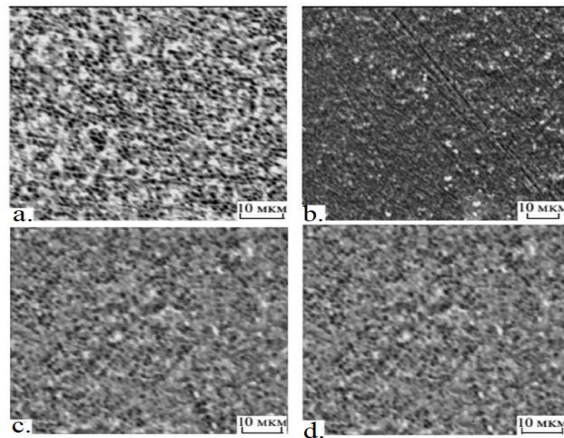

Figure 1. SEM image of the surface after etching of a por -Si sample with deposited metals: por-Si (a); por-Si (Fe) (b); por-Si(Co) (c); por-Si(Ni) (d).

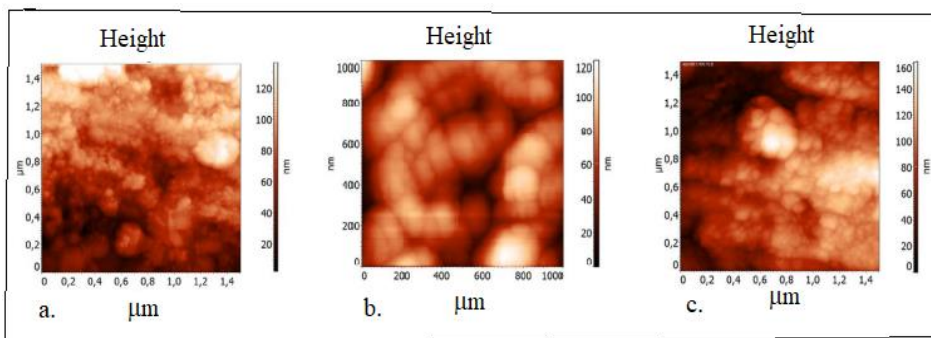AFM images of porous silicon samples with galvanically deposited modes

Figure 2. AFM topography images, dz=120nm, of samples a) por-Si:Fe, b) por-Si:Co, c) por-Si:Ni.

were obtained using the atomic force microscopy method of the Ntegra nanolaboratory Terma "LETI" in semi-contact mode and using a magnetic probe. According to the study of the surface relief of the samples using atomic force microscopy in the semi-contact mode (Figure 2), it can be seen that etching reveals the direction of grinding of silicon wafers, a quasi-periodic texture with pores with a diameter of about 50–200 nm is formed, which is consistent with the SEM data. The surface of the studied mesoporous silicon is characterized by height differences up to 200 nm.

3. Results and discussions

Figure 3 shows the PL spectra of por-Si and por-Si samples with deposited 3d metals when excited by a gas discharge lamp with a wavelength of 250 nm at room temperature (exposure to the atmosphere for 6 months). It should be noted that a smaller excitation wavelength corresponds to a smaller depth of analysis. Thus, for crystalline silicon, the depth at which the intensity of the exciting radiation drops by a factor of e for sources of exciting radiation with λ = 250, 337, and 650 nm is approximately 5 nm, 10 nm, and 3 μm, respectively.
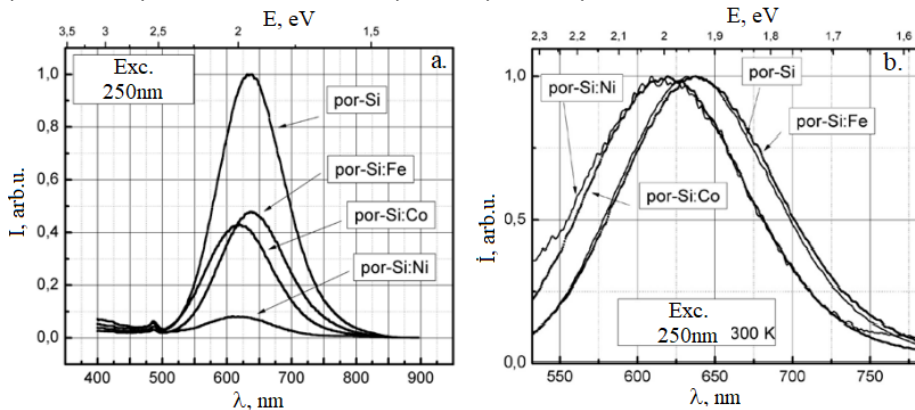

Figure 3 PL spectra of por-Si samples with deposited 3d-metals (excitation source λ = 250 nm, exposure to the atmosphere for 6 months), b) the same spectra normalized to unity

Six months after the preparation of the composites, the PL intensity of the samples with deposited metals is lower than for the initial porous silicon. This can be promoted by the formation of an island film on the surface, which can reflect part of the exciting radiation. In addition, from the point of view of the exciton mechanism of PL in porous silicon [5], when a metal is introduced into pores, a local charge redistribution can occur, and, as a result, the Coulomb forces binding

the exciton change. As a result, excitons are screened, and the PL intensity decreases. It can also be assumed that the lifetime of the radiative recombination of excitons decreased in the samples with deposited 3d metals. The normalized photoluminescence spectra of samples of the original porous silicon and por-Si with deposited Fe, Co and Ni are shown in Figure 3 b. The position of the PL peak of the samples with Co and Ni shifted somewhat (~0.1 eV) toward shorter wavelengths relative to por–Si and por–Si:Fe, which can be caused by changes in the PL mechanism.

Figure 4. shows the photoluminescence spectra of porous silicon samples with deposited and co-deposited iron and cobalt when excited by a source with a length waves λ = 337 nm. Exposure of the samples to the atmosphere prior to shooting was 10 days and 6 months.

The PL bands of the nanocomposites are almost identical in width and slightly differ in intensity and location of the photoluminescence peak. For all nanocomposites, the PL peak is located in the region of 650–660 nm, corresponding to energies of 1.8–1.9 eV. The PL peak of the porous silicon sample with cobalt deposited por-Si:Co (660 nm) is shifted relative to the peak sample with iron-deposited por-Si:Fe (650 nm) towards longer wavelengths (lower excitation energies), while the position of the PL peak of all samples obtained by co-deposition of these metals is in the wavelength range between the PL peaks of the por-Si:Fe and por Si:Co samples. Figure 4. b shows the photoluminescence spectra of por-Si samples with deposited metals, kept in the atmosphere before shooting for 6 months (excitation source λ = 337 nm).

A comparison of the spectra in Figure 4. shows that with an increase in the exposure of samples to the atmosphere, for a number of samples, a shift in the photoluminescence peaks in towards shorter wavelengths (higher energies) from 650–660 nm (1.8–1.9 eV) to 600–640 nm (1.9–2 eV), which is characteristic of porous silicon. There is also a change in the PL intensity samples relative to each other, while the most intense PL among other samples is in the por-Si:3Co7Fe sample, the position of the PL peak of which changes with time slightly (from 660 nm to 650 nm). Thus, it was found that the joint deposition of metals from a solution of 30% Co sulfate + 70% solution of Fe sulfate on the surface por-Si contributes to a better preservation of the intensity of its photoluminescence over time than the deposition of only one of the metals or their mixtures in other proportions. Should It should be noted that both iron and cobalt form deep levels in the band gap of silicon and silicon oxide [6].

The photoluminescence kinetics of the studied samples of the initial porous silicon and silicon with deposited 3d-metals was also recorded 6 months after the samples were obtained on an MDR-12-1 LOMO monochromator with a

HAMAMATSU PMT. The linear portions of the kinetics were approximated by an exponential, as a result of which graphs of the dependence of the exciton lifetime on the photoluminescence wavelength were obtained.
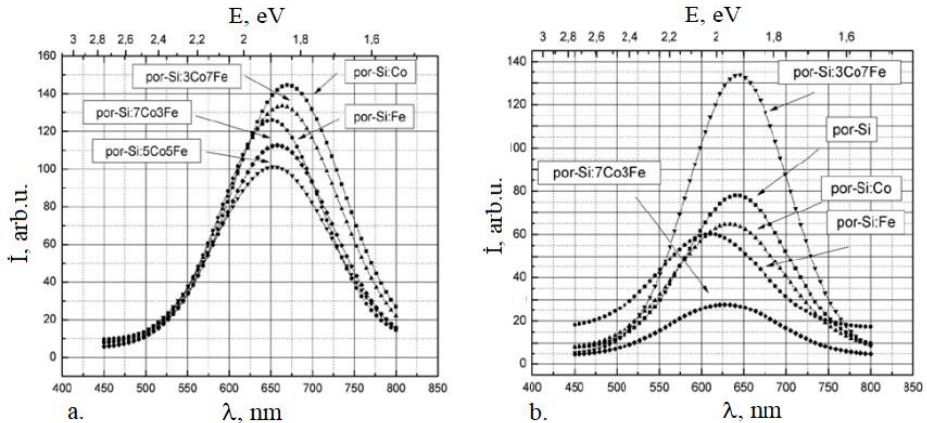

Figure 4. Photoluminescence spectra of samples of 3d-metal nanocomposites based on porous silicon, ist. excitation λ = 337 nm. Exposure time in the atmosphere a) 10 days, b) 6 months.

It has been established that, by changing the type of deposited metal into a solid-state matrix of porous silicon, one can change the intensity and peak positions of the PL spectra, change radiative lifetime of excitons. An analysis of the PL excitation spectra confirmed the conclusion about the change in the radiative lifetime of excitons in porous silicon samples with deposited 3d metals compared to the initial por-Si sample. It has been established that the joint deposition of metals from a solution of 30% Co sulfate + 70% solution of Fe sulfate on the surface por-Si contributes to a better preservation of the intensity of its photoluminescence over time than the deposition of only one of the metals or their mixtures in other proportions.

4. Conclusion

Thus, photoluminescence studies show that the optical properties of nanocomposites based on porous silicon with ferromagnets can be changed by introducing a certain transition metal or mixture of metals into the porous silicon matrix. This indicates the promise of this approach in the creation of new devices for recording information and metamaterials.

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