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RAMAN AND PL INVESTIGATION of LIGHT-EMITTING NC-Si-SiO$_x$ NANOSTRUCTURES

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ABSTRACT

The effect of HF vapor treatment on the characteristics of porous oblique deposited and annealed at temperature of 975°C SiO$_x$ films have been studied by Raman spectroscopy and photoluminescence (PL) measurements. It was shown that high-temperature annealing results in the decomposition of SiO$_x$ and the formation of amorphous Si nanoclusters embedded in the oxide matrix. The obtained nc-Si-SiO$_x$ structure is characterized by PL with a peak at the wavelength 820 nm. As a result of HF vapor treatment, considerable PL intensity growth and blueshift of PL peak position are observed. Raman measurements indicate also on substantial reduction of strain in the nc-Si-SiO$_x$ films caused by HF treatment. It is suggested that the evolution of the PL spectra in HF vapor-treated samples can be attributed to the selective-etching-induced decrease in the Si nanoparticle dimensions and the passivation of Si dangling bonds (that are nonradiative recombination trap states) by hydrogen and oxygen.

The possibility to control the PL characteristics (peak position and intensity) of the light-emitting nc-Si–SiO$_x$ structures in a wide range by above treatments is shown.

Key words: nanoclusters, silicon oxide, photoluminescence, Raman spectroscopy, thin film.

INTRODUCTION

Thin-film structures containing Si nanoclusters (nc-Si) embedded in the SiO$_x$ matrix attract the attention of many researchers, because of their promising applications in advanced electronic and optoelectronic devices [1, 2]. The structure of the Si nanoparticles depends on the formation temperature: annealing at temperatures below 900°C results in formation of amorphous inclusions, whereas at higher temperatures the Si nanocrystals are formed. The photoluminescence (PL) emission in such systems consists of an intense and wide band peaking in the near-infrared or visible spectral range in depending from nanoclusters structure and size. With decreasing nc-Si dimensions, the emission peak shifts to shorter wavelengths of the spectrum. The some peak shift is observed with transition from crystalline to amorphous nanoinclusions in the SiO$_x$

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matrix [3].

The most important factors influencing the characteristics of PL are nanoparticle size and state of the nanoparticle–SiO_x interface. The control of nc-Si size and passivation of nonradiative states and defects at this interface is an essential requirement in order to increase the intensity of PL. The Si–SiO_x interface can be modified by chemical compounds of necessary composition. Such treating is most efficient in porous structures and at enhanced pressure and temperature [4].

Recently, [5], we have proposed the method of porous nc-Si-SiO_x light-emitting structure formation using oblique deposition of Si monoxide (SiO) in vacuum. The electron microscopy studies show that, during such deposition, SiO_x films with a porous (column-like) structure are formed, with the column diameter depending on the deposition angle. During high-temperature annealing of such films, the thermally stimulated formation of Si nanoinclusions occurs in a restricted volume of the SiO_x columns. This method allows high-precision control of the thickness and porosity of the films.

Because of free space (cavities) between the oxide columns, such structures is more susceptible to chemical treatments, e.g., to treatment with acetone or ammonia vapors, or etching in HF solution [6, 7]. Such treatments modify the nc-Si/SiO_x interface, nanoparticle size and, thus, influence the light-emission properties.

In this paper we investigate the effect of chemical treatment in the HF vapors on the PL and Raman spectra of the porous light-emitting nc-Si–SiO_x structures, produced by oblique deposition in vacuum.

EXPERIMENT

The thin-film SiO_x samples were fabricated by thermal evaporation of 99.9% pure silicon monoxide SiO (Cerac Inc.) in vacuum ((1–2) $\times 10^{-3}$ Torr) onto two-side polished Al_2O_3 or Si substrates. During deposition, the substrates were oriented at an angle of 60° between the normal to the substrate surface and the direction to the evaporator. The evaporation rate was monitored in situ by the quartz-crystal-oscillator monitor system (KIT-1). The film thickness measured with the use of an MII-4 microinterferometer after deposition was 0.8-1.0 μm.

Because of additional oxidation by residual gases during evaporation of SiO, the compositionally nonstoichiometric SiO_x ($x > 1$) films were deposited in the vacuum chamber. The films were annealed in vacuum during 15 min at temperature of 975°C. Such high-temperature annealing results in the decomposition of SiO_x and the formation of Si nanoclusters embedded in the oxide matrix (nc-Si-SiO_x structure) [1,2].

Annealed nc-Si–SiO_x samples were placed in closed cell with HF vapor flow at temperature 30°C. Treatment in HF vapor results in selective etching of

SiO_2 inclusions in porous heterogeneous nc-Si-SiO_x structure.

The PL spectra were recorded at room temperature in the wavelength range from 440 to 900 nm using 337 nm line of a nitrogen laser as excitation source. These spectra were normalized to the spectral sensitivity of the experimental system. The Raman spectra were registered at a room temperature using Jobin-Yvon T64000 spectrometer equipped with a CCD detector. For excitation of the spectra the 488.0 nm line of the Ar laser was used.

RESULTS AND DISCUSSION

Results of SEM investigations of oblique deposited SiO_x samples (*Figure 1*) were shown in the previous papers [5,7]. Such films have a porous (inclined column-like) structure with the column diameter varies in the range 10-100 nm. The dimensions of the columns, their orientation, and the porosity (the relative volume of pores) of the films depend on the angle of deposition. The porosity of samples deposited at β = 60°, is equal to 34 % [8], the parameter x in the SiOx films was 1,73 before annealing and close to 2 after annealing at 975°C[9]. High-temperature annealing of oblique deposited SiO_x films do not change porosity and column-like structure of the samples.

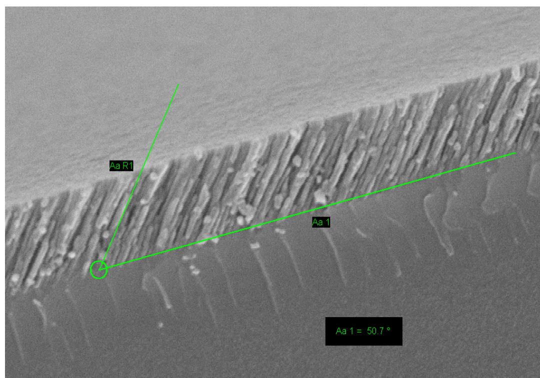

Fig.1 – Electron microscopic image of oblique deposited SiO_x films

The normalized PL spectra of the nc-Si–SiO_x samples deposited onto Si substrates, then annealed and HF vapor treated are shown in *Figure 2*. The emission spectrum of the initial annealed but unetched sample (curve 1) exhibits a broad band, with a peak at the wavelength 820 nm in the near-infrared region. Curves 2, 3, and 4 in *Fig. 2* correspond to the samples etched in the HF vapor during 1.5, 10, and 30 min, respectively. With increasing time of etching, we observe a gradual shift of the emission peak to shorter wavelengths and increasing of the PL intensity. Specifically, after etching during 10 min, the peak of the PL band is at about 700 nm and the intensity of PL peak becomes near 200 times of magnitude higher then the emission intensity of the initial annealed sample. The further increase in the time of etching of the samples ($t > 10$ min) is accompanied by a further short-wavelengths shift of the emission bands and gradual decreasing of emission intensity.

The evolution of the emission bands can be attributed to the etching induced decrease in the *nc*-Si dimensions (from ~ 3.8 to 2.4 nm [10]) and to the effect of quantum confinement of charge carriers in the nanosized structures. In the porous nc-Si–SiO_x samples HF vapor penetrates deep into the entire film and dissolves SiO_2 at the surface of the oxide columns, thus stripping nc-Si. After HF treatment, the nc-Si newly forms a thin native oxidized layer on the surface when exposing it to atmospheric oxygen. Because of oxidation of the nc-Si surface, dimensions of the initial nc-Si core are reduced, resulting in the blueshift of the emission spectrum. Huge enhancement in the PL intensity of about two hundreds times during HF vapor treatment can be related to the passivation of Si dangling bonds (that are nonradiative recombination trap states) by hydrogen and oxygen.

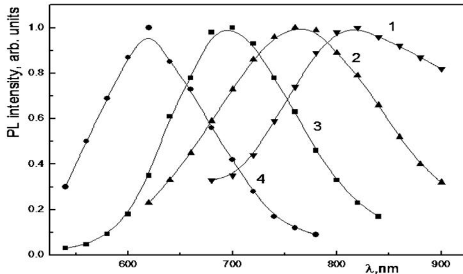

Fig. 2 – Normalized room temperature PL spectra of the nc-Si–SiO_x samples annealed at 975°C (curve 1), then HF vapor treated during 1.5 (curve 2), 10 (curve 3), and 30 min (curve 4)

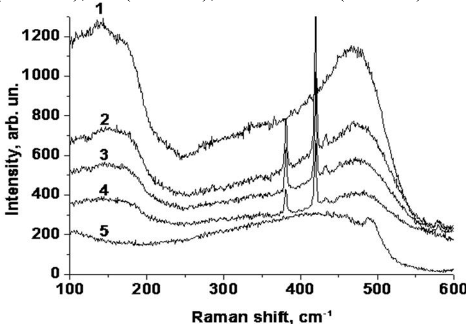

Fig. 3 – Raman spectra of the nc-Si–SiO_x samples annealed at 975°C (curve1), then HF vapor treated during 5 (curve 2), 10 (curve 3) and 30 (curve 4) min, accordingly, and reference spectrum from SiO_2 film (curve 5)

Figure 3 presents Raman spectra of the SiO_x films deposited onto Al_2O_3 substrates (reference samples) as-annealed at 975° C (nc-Si–SiO_x samples) on (curve 1), then HF vapor treated during 5 (curve 2), 10 (curve 3) and 30 (curve 4) minutes, respectively. The typical for amorphous silicon peaks (TA (~ 145 cm^{-1}), LA (~ 305 cm^{-1}), LO (~ 365 cm^{-1}), TO (~ 475 cm^{-1})) show up in all spectra. In the spectra for HF vapor treated films four narrow peaks with frequencies 381, 420, 433 and a 579.5 cm^{-1} were appeared. Such modes are characteristic for sapphire substrate. With the increase of treatment time intensity of these peaks grows, that testifies to reduction of nc-Si–SiO_x film thickness. With the increase of HF treatment time the TO mode shift to high-frequency side and for the sample treated for 30 minutes such shift is equal to ~ 8 cm^{-1}.

It can indicate on substantial reduction of strain in the films caused by passivation of the Si dangling bonds on the nc-Si surface with the hydrogen and oxygen atoms. Detecting of silicon nanocrystals by Raman measurements at these research conditions was not succeeded.

It should be mentioned, that semiwidth of TO - bands after HF vapour treatment of nc-Si–SiO_x samples does not change. It is known, that semiwidth of TO-bands is determined by dispersion of bond angles between atoms, i.e. by fluctuations in the nearest order [11]. It means, that during HF treatment no additional structural rearrangement in amorphous Si clusters does not take place.

CONCLUSIONS

In this study it was shown that:

a) High-temperature annealing of the SiO_x films at temperature of 975°C. results in their decomposition and formation of amorphous Si nanoclusters embedded in the oxide matrix.

b) The obtained nc-Si-SiO_x structure is characterized by PL with a peak at the wavelength 820 nm.

c) As a result of HF vapor treatment an increase in the PL intensity and a spectral shift of the PL peak to shorter wavelengths (maximum blueshift more then 200 nm) are observed, that correspond to change of amorphous Si nanoclusters size from ~ 3.8 to ~2.4 nm.

d) The obtained results show that by the HF vapor treatment of light-emitting porous nc-Si-SiO_x structures it is possible to control PL intensity and peak position in a wide range.

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