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Study of photoluminescence in gadolinium chloride treated porous silicon structures

R. JARIMAVIČIŪTĖ-ŽVALIONIENĖ[a,b*], S. TAMULEVIČIUS[a,c], V. ANINKEVIČIUS[d], V. GRIGALIŪNAS[c], R. TOMAŠIŪNAS[e]

[a] *Department of Physics, Kaunas University of Technology, Studentu 50, 51368 Kaunas, Lithuania*
[b] *Faculty of Technology, Kaunas College, Pramones str. 20, 50468 Kaunas, Lithuania*
[c] *Institute of Physical Electronics of Kaunas University of Technology, Savanoriu 271, 50131 Kaunas, Lithuania*
[d] *Semiconductor Physics Institute, A. Gostauto str. 11, LT-01108 Vilnius, Lithuania*
[e] *Institute of Materials Science and Applied Research, Vilnius University, Saulėtekio 10, 2040 Vilnius, Lithuania*

We report the study of photoluminescence in porous silicon treated with gadolinium chloride ($GdCl_3$), and also in as grown porous silicon. The concentration of the gadolinium on the surface of the porous silicon was determined using an "Inductively Coupled Plasma Mass Spectrometer". The photoluminescence measurements were carried out using a custom made system with a 300 nm light source. The photoluminescence intensity was enhanced drastically in $GdCl_3$ treated porous silicon samples, and was a function of the gadolinium concentration in the porous silicon layer. However, the photoluminescence was quenched when the samples were left in room ambience for several months. The rate of quenching remained almost the same in gadolinium treated porous silicon and in the as grown samples.

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1. Introduction

Porous silicon (PS) surface chemistry is crucial and of fundamental technical significance, because of its role in modern technology. Porous silicon has potential applications as chemical sensors, biosensors, opto-electronic devices such as electro-luminescent displays, photo-detectors, and photo-pumped tuneable lasers [1-4]. Therefore, modification and characterization of the porous silicon surface has become an area of intense interest [5,6]. The photoluminescence (PL) intensity and its spectral distribution are highly dependent on the chemical nature of the surface, that changes with the environmental and storage conditions. For example, when the PS is in an oxidizing ambient, the PL intensity is quenched. Although PS has a strong luminescence, the spectrum is broad and therefore not very suitable for potential light emitting device applications. Doping can change the optical properties of porous silicon, producing a narrower bandwidth luminescence spectrum. In the recent past, rare-earth doped or treated porous silicon layers have aroused great interest, due to the possibility of making LEDs, optical wave-guides, optical amplifiers etc. Several methods, e.g., co-deposition, ion-implantation, electro-chemical deposition, magnetron sputtering, spin coating etc. have been used for the doping or surface treatment of PS with rare earth elements, and to study the effect of these earth elements, particularly the lanthanides; lanthanum, europium, gadolinium, terbium, holmium, erbium, ytterbium on the PS properties [7-16]. However, most of these methods are expensive, time consuming and have compatibility problems with silicon IC processing technology. For example, ion-implantation, though very precise, can generally only be applied to a small area and the implantation time can be several hours. On the other hand, impregnation or immersion of PS layers in a halide (e.g., chloride) solution of rare earth elements can be applied to a large area in a shorter time, and is compatible with existing semiconductor processing technology. It has been used to created RE/PS structures where RE stands for lanthanides, namely terbium (Tb^{3+}), europium (Eu^{3+}), erbium (Er^{3+}) and ytterbium (Yb^{3+}).

The present paper deals with the treatment of porous silicon layers with a gadolinium containing solution, resulting in the enhancement of the luminescence and its stability.

We report the experimental study of photoluminescence in as-grown porous silicon and in PS layers treated with gadolinium chloride ($GdCl_3$). A marked enhancement in the PL was observed in a Gd treated PS layer, compared to the as-grown porous silicon sample. From the present study, however, the origin of the enhanced excitation is not yet clear and needs further investigation.

2. Experimental

In the present study, 1-1.5 Ω-cm n-type (100) silicon wafers were used. The porous silicon was formed using ethanolic HF solution ($HF:C_2H_5OH::1:1$), using an ultrasonically enhancement electrochemical bath operating

at 4.4 mW power (at 22 kHz). The porous silicon samples were made at different current densities ranging from 30 to 250 mA/cm^2. The contact on the back side of silicon was made of InGa alloy and was backed by an aluminium ring to make contact only on the periphery of the wafer. This structure was chosen in order to illuminate the sample from the backside through the hole in the aluminium ring. After completing the anodisation process, the samples were washed in deionized water (15 MΩ), followed by drying. The dried samples were immersed in a solution consisting of gadolinium chloride and hydrochloric acid. The immersion (often called i.e. treatment) time was varied from 4 to 18min, after which the samples were rinsed in DI water and dried. The samples which were treated with the Gd containing solution will be referred as PS-Gd and the as-grown samples will be referred as PS in the subsequent text.

The microstructures of the porous silicon specimens were investigated using a JEOL JSM-IC25S scanning electron microscope (SEM).

The photoluminescence was measured using a custom made system with a 300 nm excitation source. The measurements were carried out in the visible and near-infrared spectral regions, using a 1000 W Hg lamp.

The presence of gadolinium in the porous silicon layers was detected by "*Inductively Coupled Plasma Mass Spectrometry*", (ICP-MS) using a laser ablation system (UP213) that operates at an excitation wavelength 213 nm and has a dwell time and an intersite pause of 20 and 10 seconds respectively, and a laser impulse time of 4 ns. The concentration of the gadolinium in the porous silicon samples was determined by comparing the data with a NIST standard reference material, SRM612. In order to reduce the experimental error, the measurements were carried out on 4 spots separated by 200 μm from each other, with a laser spot size of 100 μm. The Gd concentration on the PS surface was calculated by following expression (1):

$$c_{Sample} = \frac{I_{Sample}}{I_{Std}} c_{Std} \qquad (1)$$

where
C_{Sample}: Gd concentration on the PS surface,
C_{Std}: Gd concentration in SRM612,
I_{Sample}: Gd intensity on the PS surface and
I_{Std}: Gd intensity of etalone SRM612.

3. Results and discussion

Fig. 1 shows an SEM picture of the microstructure of a porous silicon layer formed at an anodisation current density of 118 mA/cm^2. It is evident from the picture that the PS has grown vertically and has a well defined edge structure. The average pore depth is 170 μm.

After PS formation, the sample was treated in an acidic $GdCl_3$ solution for different times from 4 to 18 minutes.

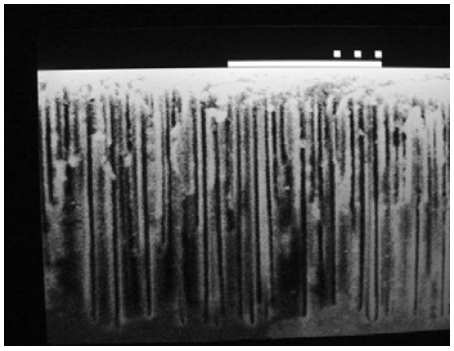

Fig.1. SEM picture showing the cross-sectional view of n-Si, electrochemically etched for 15 min at 118 mA/cm^2.

Fig. 2a shows the peaks of the Gd isotope 155 in the porous silicon samples (PS-Gd), which was detected by ICP-MS. The PS-Gd data were compared with a standard reference material SRM612 (NIST, USA), as shown in Fig. 2b. The relative surface concentration of Gd was calculated using eq. (1), and was 7.48 × 10^{-9} mg/kg for 18 min Gd treatment.

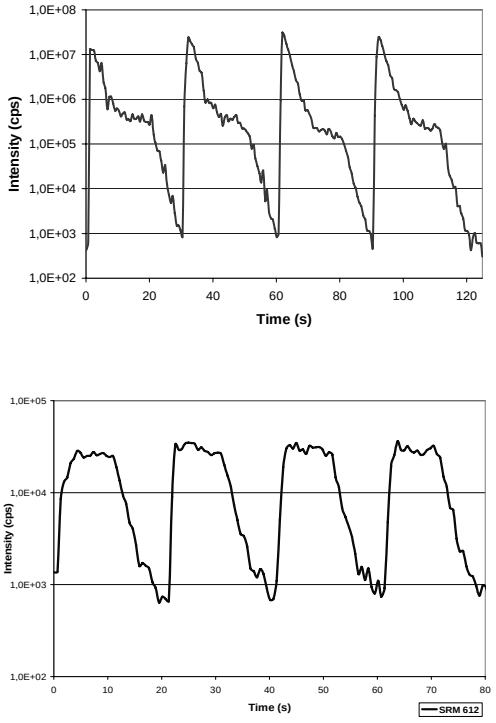

Fig. 2. Peaks of the Gd (isotope 155) in (a) a PS sample and (b) a PS-Gd sample.

The photoluminescence intensity as a function of wavelength for PS-Gd samples treated for different durations in a $GdCl_3$ solution (4, 6, 8, 12, 18 min) is shown in Fig. 3. The PL measurements were also carried out for as-grown porous silicon (sample PS) for comparison, and the data are plotted in the same figure. It is clear that the PL signal in the PS-Gd is much larger compared to the as grown (PS) sample. The PL intensity is greater in samples

treated for larger time durations (e.g. ~150 000 and ~225 000 A.U. for 4 and 18 min treatments respectively). A faint blue shift was observed in the samples treated for longer times in the Gd containing solution.

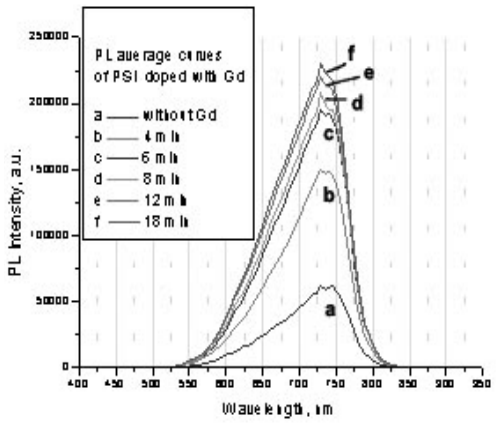

Fig. 3.Photoluminescence intensity vs wavelength in samples treated in ethanolic $GdCl_3$ solution for different times.

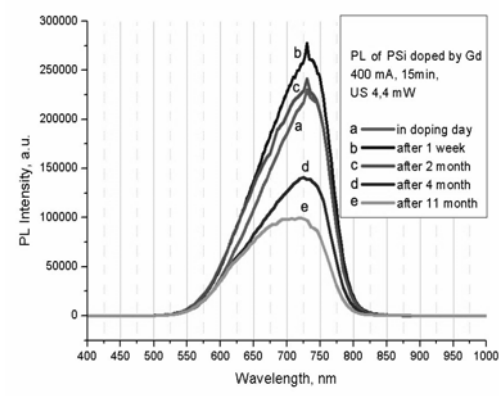

Fig. 4. PL intensity vs. wavelength in PS-Gd for different storage time depicting the quenching.

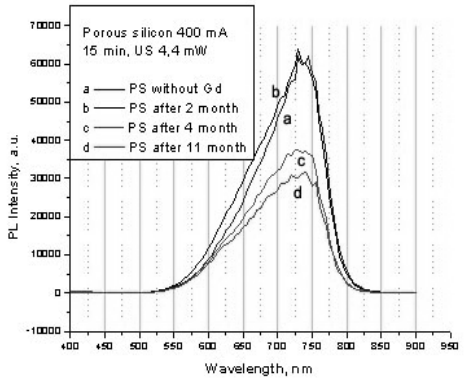

Fig. 5. PL intensity as a function of wavelength in an as-grown sample (PS) for different storage times.

Figs. 4 and 5 shows the effect of storage time on the PL intensity in the PS and PS-Gd samples respectively. After PL measurements, the samples were left in room ambience for different durations. It was observed that the PL signal was quenched in both the samples, with increases in storage time. For example, after 11 months the PL intensity fell to one third of its original value in the case of PS-Gd, whereas it fell by 50% in the case of the PS.

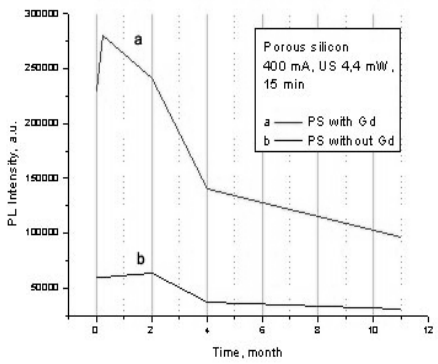

Fig. 6. Peak PL intensity vs. storage time in PS-Gd (Gd treated) and PS (as grown) samples when left in a room ambient.

Quenching in as-grown porous silicon samples has also been reported earlier by several investigators [5,6]. For clarity, the peak (maximum) values of the photoluminescence are plotted as a function of storage time for the PS PS-Gd in Fig.6. As mentioned above, the quenching was observed in both the as-grown PS sample and the Gd treated porous silicon with storage time. However, the rate of quenching was different in the two cases. The present study shows that that PL can be enhanced dramatically in porous silicon treated with gadolinium; however, stability remains a problem that requires further investigation.

4. Conclusions

Porous silicon was made using an ultrasonically enhanced electrochemical etching system, and the PS samples were treated in an acidic solution containing gadolinium for different durations.

The concentration of the gadolinium isotope 155 in Gd-treated porous silicon samples was determined by "Inductively Coupled Plasma Mass Spectrometry", and was found to be 7.48×10^{-9} mg/kg. The presence of gadolinium in the porous silicon structure significantly enhanced the photoluminescence (three times in magnitude) compared to that in untreated as-grown samples. However, the PL signal quenched when samples were left in room ambient, and depended strongly on the storage time. The noticeable difference during quenching was that the PL values were always more in PS-Gd samples than in the untreated porous silicon. It can be concluded from the present study that PL can be enhanced drastically by the incorporation of Gd on a PS surface.

Acknowledgements

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*Corresponding author: renata@kauko.lt