

Photoluminescence Properties of LaF₃-Coated Porous Silicon

Sinthia Shabnam Mou, Md. Johurul Islam, Abu Bakar Md. Ismail*

Department of Applied Physics and Electronic Engineering, Rajshahi University, Rajshahi, Banglaesh.
Email: ismail@ru.ac.bd

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ABSTRACT

This work reports the coating of porous silicon (PS) with LaF₃ and its influence on the photoluminescence (PL) property of PS. PS samples, prepared by electrochemical etching in a solution of HF and ethanol, were coated with e-beam evaporated-LaF₃ of different thicknesses. It was observed that the thin LaF₃ layer on PS led to a good enhancement of PL yield of PS. But with the increasing thickness of LaF₃ layer PL intensity of PS was decreasing along with a small blue-shift. It was also observed that all the coated samples showed degradation in PL intensity with time, but annealing could recover and stabilize the degraded PL.

Keywords: Porous Silicon, Anodic Etching, Photoluminescence, Surface Coating, Photonics

1. Introduction

Porous silicon (PS) can be considered as a silicon (Si) crystal having a network of voids in it [1]. The nanosized voids in the Si bulk result in a sponge-like structure of pores and channels surrounded with a skeleton of crystalline Si nanowires. Because of its versatility and tunable characteristics, PS has attracted much attention in optoelectronic industry due to its considerably strong photoluminescence (PL) behavior at room temperature apart from its various applications such as sensor and MEMS. As it has a potential to emit visible light, it is expected that this material can be effectively used to fabricate Si-based visible light emitting devices and optical interconnections. The PL phenomena of PS were reported in the red light region first, while orange, yellow and green PL was also observed latter. The wide spectral tunability of the PL of PS that extends from near infrared (IR) through the whole visible range to the near ultraviolet (UV) make this material a very interesting one. A disadvantage of this material is the aging, that is, the slow spontaneous oxidation of PS [2]. A native oxide layer forms on the surface of the pores and the thickness of this oxide layer grows with time. Due to the aging effect, the structural and optical properties of PS show continuous change with storage time [2]. That is, many of its properties, such as PL, are age dependent and unstable, and why PS is still can not be applied in photonics. One possible way to reduce the aging effect could be “passiva-

tion” of PS [3]. This surface coating can be achieved from various chemical adsorbates by several techniques [4-6].

In this work, an attempt has been made to coat PS surface by Lanthanum Fluoride (LaF₃), aiming to obtain stable and enhanced luminescence of PS layers. LaF₃ is a large band-gap (about 10.3 eV) [7] material having a hexagonal crystal structure with a refractive index of 1.61 [8]. Lanthanum fluoride is a promising vacuum ultraviolet (VUV) transparent material similar to the other large band-gap fluorides such as GdF₃ and MgF₂. Due to its high band-gap and refractive index, higher than those of the other VUV transparent films, LaF₃ is a useful material for VUV optics. Therefore, the PL properties of anodically etched PS with and without LaF₃-coating have been compared and the influence of LaF₃-coating on the PL has been discussed in this article. The experimental results show that coating the PS with optimum LaF₃ thickness could provide stabilization of PL of PS, which is very important for PS to be a potential material in photonic devices.

2. Experimental

PS was prepared by anodic etching of p⁺-type single crystal silicon wafer having <100> orientation, 10 - 24 Ω cm resistivity and 200 ± 20 μm thickness. Etching was done in a 3:1 (v/v) solution of 48% HF and absolute ethanol. PS samples with various current densities and

etching times were prepared. Among them, the samples with 15 mA/cm² current density and 10 min etching time were coated with LaF₃ of three different thicknesses (70 ± 10 nm, 120 ± 10 nm and 180 ± 10 nm). The etching or electrochemical dissolution of Si wafer was done using single tank cell arrangement, where the Si itself was used as the anode and a platinum (Pt) electrode was used as the cathode. The back contact of the Si wafer was done by depositing a thick silver (Ag) layer by electron-beam (e-beam) evaporation. The anhydrous LaF₃ with 99.999% purity was bought from the Kishida Co., Japan, and was used without further purification. LaF₃ layers were deposited by e-beam evaporation in a vacuum coating unit. A high vacuum of 10⁻⁶ Torr was maintained during evaporation of LaF₃. PL study was done by Spectro Fluorophotometer where the excitation wavelength was 350 nm.

Just after anodic etching the PS samples were dried and put inside the vacuum coating unit for LaF₃ deposition.

3. Results and Analysis

The fabricated PS samples with LaF₃ layers were investigated with a scanning electron microscope (SEM). **Figures 1** and **2** show the SEM image of the surface and cross-section of a LaF₃-coated PS sample with a 180 ± 10 nm LaF₃ layer. Since LaF₃ covers the whole surface the pore tips are not visible. The LaF₃/PS/Si heterostructure (from left to right in the image) is clearly visible in **Figure 2**. For both sets of the as-grown PS sample, single PL peak appeared around 695 nm, which is similar to the reported value [9,10]. The oxygen content of the film was very low which is evident from the single-peak PL band of PS [11]. The PL spectra of PS coated with LaF₃ layer of three different thicknesses with an uncoated PS sample has been compared and shown in **Figure 3**.

It is clearly seen from the figure that coating PS with thin (e.g. 70 nm) LaF₃ layer could protect the PS from its PL intensity-degradation, which may be related to the coating effect of the LaF₃ that prevents the PS surface chemistry. But with the increase in the thickness of LaF₃, the PL intensity is decreased. And for the sample with LaF₃ of 180 ± 10 nm thickness, the PL intensity of PS is decreased even below the PL intensity of the uncoated PS. The decrease in the intensity of the PL emission with increasing thickness of LaF₃ can be explained by the absorption of light by the LaF₃ shell. The light emitted by the PS is absorbed by the LaF₃ when it passes through the LaF₃ layer. The absorption is proportional to the thickness of the LaF₃ layer. Therefore, the intensity of the PL emission decreases with the increase of the LaF₃ thickness. The important thing is the shape of the PL response that did not change due to coating with LaF₃.

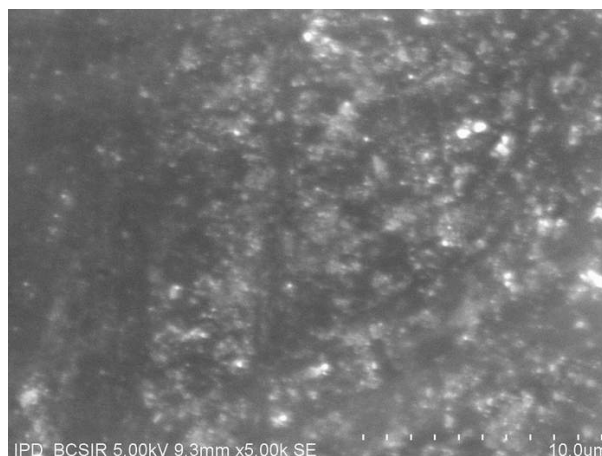


Figure 1. SEM image of LaF₃-coated PS surface.

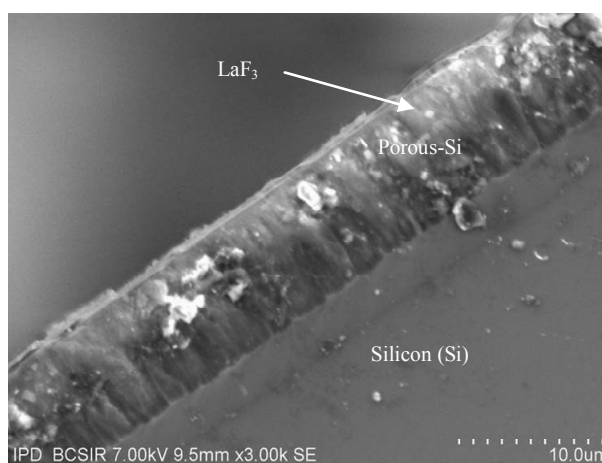


Figure 2. Cross-sectional SEM image of PS sample coated with LaF₃.

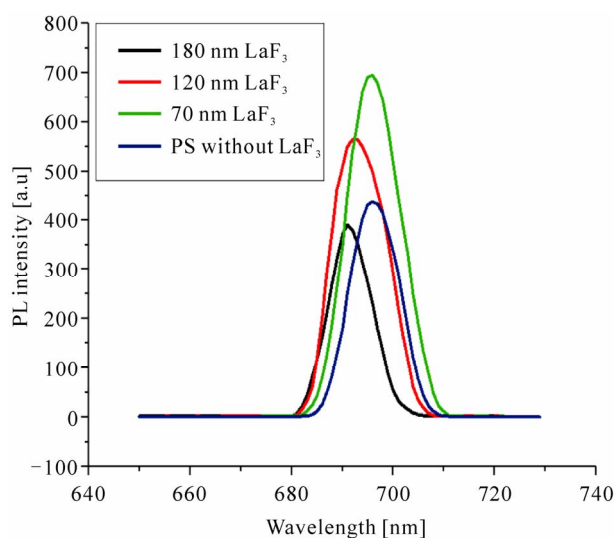


Figure 3. Comparative PL spectra of PS with and without LaF₃ coating.

The full width at half maxima (FWHM) of the Gaussian shaped PL response of the coated-PS remained almost constant at ~ 12 nm. This signifies that the LaF₃ layer behaves just as a capping layer that keeps the Pb-center of PS and do not interfere with the PS surface chemistry inside the pore.

The peak wavelengths of the PL spectra of the samples shifted a little towards blue with the increasing thickness of LaF₃. This nature of blue-shift has also been reported by Gokarna *et al.* [12] for the PS/CdS and ZnS system. This shift in the wave length of the PL can be attributed to the shrinking of nanocrystallites due to thicker LaF₃ layer [13]. The shift has been shown in **Figure 4**. The FWHM of the PL responses of the LaF₃-coated PS was very narrow (~ 12 nm) that implies the homogeneity of the nanocrystal.

LaF₃-coated PS samples were then stored in air for one month and the aging effect on the PL intensity was observed. It was observed that the PL intensity of LaF₃-coated PS also decreased due to the aging effect (**Figure 5**). But all the three samples did not show same amount of degradation in PL intensity. PS sample coated with LaF₃ of less thickness (70 ± 10 nm) suffered more from aging effect than those coated with thicker LaF₃, *i.e.* the lower the thickness of LaF₃, the more was the aging effect.

It appeared from the SEM that the LaF₃ layer only deposited as a capping layer and did not deposit into the pore of the porous silicon to passivate the silicon skeleton. The aging effect of the LaF₃-coated PS may be due to the trapped oxygen in the pore of the porous silicon that slowly oxidizes the silicon skeleton. As-deposited LaF₃ layer shows non-stoichiometry [14] and reach in pores [15]. The thicker layer of the LaF₃ could provide protection from the further oxidation of the silicon skeleton from the ambient oxygen, but the thinner layer failed because of pores in the LaF₃. That is why the degradation in the PL intensity was more for the thinner layer of as-deposited LaF₃ on PS.

But these pores can be removed, and stoichiometry of LaF₃ layer can be partially recovered by annealing that may cause the PL stabilization of PS. The degradation of PL and recovery of PL has been compared in the **Figure 6**. As shown in **Figure 6**, annealing recovers the PL intensities for all the coated samples. The influence of annealing on the PL of LaF₃-coated PS will be reported elsewhere.

4. Discussion

Coating of PS with e-beam evaporated LaF₃ has been investigated for the first time in order to see the role of LaF₃ as a coating layer on the optical properties of PS such as, in enhancing and stabilizing the PL of PS. The

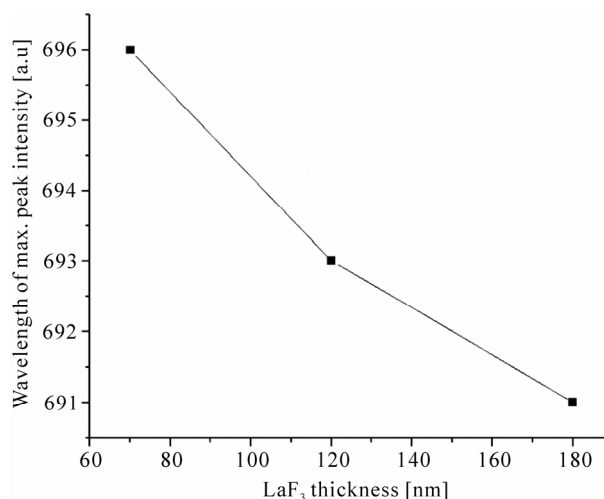


Figure 4. Small blue-shifts with the LaF₃ thickness.

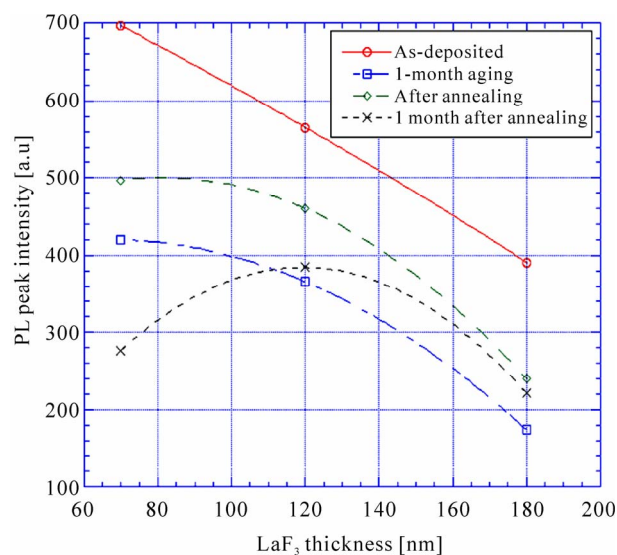


Figure 5. Aging of PL intensity of LaF₃-coated PS with time.

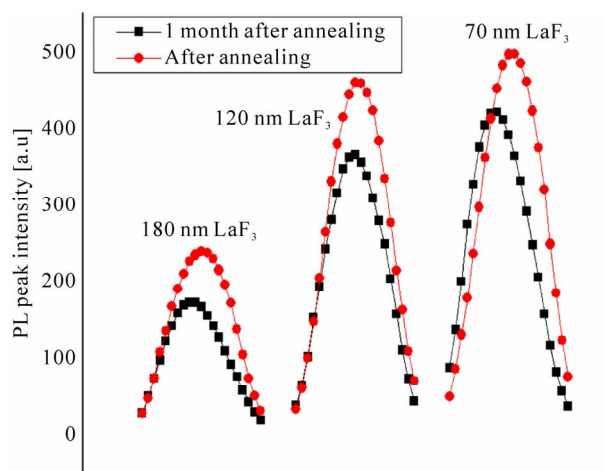


Figure 6. Partial recovery of PL intensity by annealing.

thickness of the LaF₃ appeared to have an important influence on the PL characteristics of PS. Thinner layer of LaF₃ could enhance the PL intensity without destroying the Gaussian shape of the PL response. This enhancement of PL is believed to be due to the coating effect of LaF₃ that prevented oxidation of PS. But thicker layer of LaF₃ lowered the PL intensity that may be due to the degradation of refractive index of the LaF₃ layer induced by the mechanical stress which depends on the film thickness. The LaF₃-coated un-annealed samples showed aging on the PL intensity. Generally the as-deposited evaporated LaF₃ layer contains pores which when exposed to the air water vapor enters into the pore due to capillarity. This water vapor replaces the Si-H bonds with Si-O bond which seems responsible for the degradation of the PL intensity. As the thicker layer of as-deposited LaF₃ contains more water vapor the degradation of PL intensity was more. When the coated samples were annealed at 400°C for 10 minutes the PL intensity was partially recovered and the degradation of the recovered PL intensity was minimum for PS cited with thicker LaF₃ layer. Experimental results suggest that coating PS with e-beam evaporated LaF₃ and subsequent annealing could enable the PS to have an enhanced and stable PL.

5. Conclusions

All the studies done in this work can be summarized as; coating PS with LaF₃ of optimum thickness followed by annealing could lead to better luminous stability of PS. From these experimental results it can be concluded that coating with LaF₃ of optimum thickness could provide the PS an enhanced and stable photoluminescence that will enable its use in the fabrication of optical devices, such as light-emitting diodes (LED), lasers and solar cells.

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