Investigation on LaF_3/porous silicon system for photonic application

Halima Khatun[1], Sinthia Shabnam Mou[2], Abdul Al Mortuza[1], and Abu Bakar Md. Ismail[1*]

[1]*Department of Applied Physics and Electronic Engineering, Rajshahi University, Rajshahi 6205, Bangladesh*

[2]*School of Electrical and Electronic Engineering, Independent University, Dhaka 1200, Bangladesh*

[*]*E-mail: ismail@ru.ac.bd*

Received September 17, 2009

We present the investigation on LaF_3/porous silicon (PS) system that has properties of both the materials to be applied in photonics. Epilayers of LaF_3 are grown on PS under different anodization conditions using electron-beam evaporation (EBE). The characteristics of the LaF_3/PS system are analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), and photoluminescence (PL). XRD confirms the polycrystalline nature of the LaF_3 film. Nearly stoichiometric growth of LaF_3 on PS is established by EDX. Such a thin LaF_3 layer grown on PS leads to a good enhancement of PL yield of PS. But with the increasing thickness of LaF_3 layer, PL intensity of PS is found to decrease along with a small blue-shift.

OCIS codes: 160.2540, 250.5230, 160.5690.

doi: 10.3788/COL20100803.0306.

Porous silicon (PS) has drawn tremendous interest of the researchers during the last decade because of its potential to emit visible light at room temperature. It is expected that this material can be effectively used to fabricate Si-based visible light emitting devices and optical interconnections. To take benefit from the intense red photoluminescence (PL) of PS at room temperature[1], many attempts have been made to introduce PS into some Si-based optoelectronic devices. A disadvantage of this material is the aging effect, 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 still cannot be applied in photonics. The efficiency of the PS-based devices could be increased strongly by passivating them with appropriate materials[3]. This tendency led to various attempts to improve the efficiency with other materials, including GaAs[4], indium tin oxide (ITO)[5], GaN[6], ZnO[7], ZnSe[8], copper films[9], and polymers[10]. Obviously, additional investigations still have to be performed to optimize the main features of the fabricated devices.

In this letter, we attempt to passivate PS surface by LaF_3, aiming to obtain stable and enhanced luminescence of PS layers. LaF_3 is a large band-gap (about 10.3 eV) material[11] which has a hexagonal crystal structure with a refractive index of 1.61[12]. It is a promising vacuum ultraviolet (VUV) transparent material similar to the other large band-gap fluorides such as GdF_3 and MgF_2. Due to its higher band-gap and refractive index than those of the other VUV transparent materials, LaF_3 is a useful material for VUV optics. Therefore, the PL properties of anodically etched PS with and without LaF_3 passivation are compared and the influence of LaF_3 passivation on the PL is discussed. The experimental results show that passivating the PS with optimum LaF_3 thickness could provide stabilization of PL of PS, which is very important for PS to be a potential material in photonic devices.

PS was prepared by anodic etching of p^+-type and n^+-type single-crystal silicon wafers with <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. The PS samples with various current densities and etching times were prepared. Three different thicknesses (70±10, 120±10, and 180±10 nm) of LaF_3 layer were grown on the PS samples prepared at a current density of 15 mA/cm^2 and etching time of 10 min. The etching of silicon wafer was done using single-tank cell arrangement, where Si itself was used as the anode and a Pt electrode was used as the cathode. The back contact of the silicon wafer was done with depositing a thick Ag layer by electron-beam evaporation (EBE). The anhydrous LaF_3 (99.99% purity, Kishida, Japan) layers were deposited by EBE at a pressure of 10^{-6} Torr using a vacuum coating unit (Edwards, UK). The PL study was done by spectro fluorophotometer (RF-5301PC, Shimadzu, Japan) with the excitation wavelength of 350 nm.

Just after anodic etching, the PS samples were dried and put inside the vacuum coating unit for LaF_3 deposition. The properties and structure of the fabricated LaF_3/PS samples were investigated by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). Figures 1 and 2 show the SEM images of the surface and cross-section of a LaF_3/PS system with a 180±10 nm thick LaF_3 layer. The LaF_3 surface is found to have a large amount of voids and cracks, but the islands has a very smooth surface with no pinholes and outgrowths on the surface, Since LaF_3 covers the whole surface, the pore tips are not visible. The LaF_3/PS/Si heterostructure (from left to right in the image) is clearly visible in Fig. 2.

Figure 3 shows the grazing incidence XRD spectra of LaF_3/PS/Si system. In order to determine and verify the phase formation of LaF_3 on PS, the XRD analyses were carried out in the 2θ range from

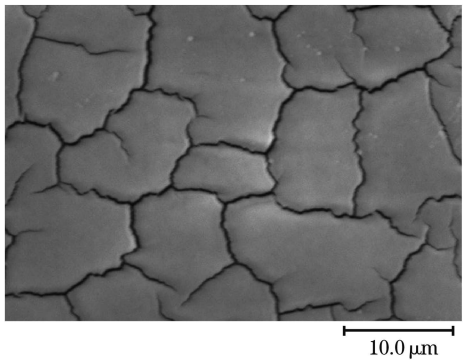

Fig. 1. SEM image of LaF_3 surface on PS.

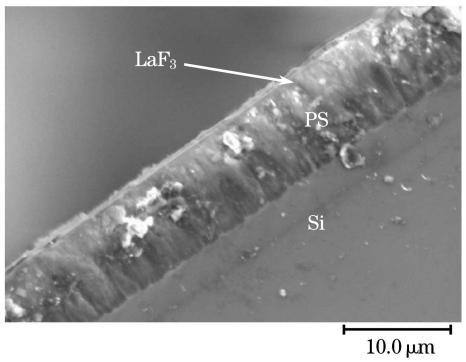

Fig. 2. Cross-sectional SEM image of PS sample passivated by LaF_3.

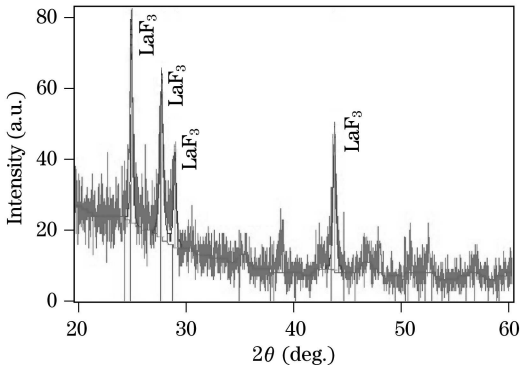

Fig. 3. XRD pattern of LaF_3 grown on PS at room temperature.

20° to 60°. This pattern confirms the phase formation of LaF_3 with a large peak centered near 27.6° corresponding to (111) crystal orientation and other relative diffusion peaks at 2θ on 24.9°, 28.9°, and 43.8° corresponding to (110), (200), and (300) crystal orientations, respectively. The positions and the relative intensities are identified from the Inorganic Crystal Structures Database (ICSD) file. The positions of these peaks closely resemble a polycrystalline hexagonal (P-3c1) structure.

The compositional analysis of the LaF_3 film on PS has been done by EDX. The result in Fig. 4 and Table 1 were obtained from EDX software. The counts in Fig. 4 were obtained after correcting the "net counts" in Table 1 with a correction factor k. k includes three different effects, namely, the effects of atomic number (Z), absorption within the sample and detector (A), and X-ray fluorescence by the sample (F). As shown in Fig. 4,

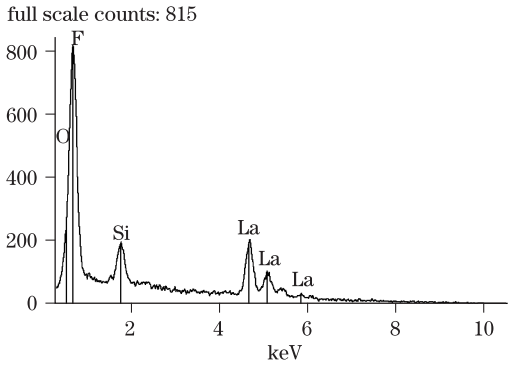

Fig. 4. EDX spectrum of the LaF_3/PS system.

Table 1. Atom Percentage of the Whole System

Element	Net Counts	Weight (%)	Atom (%)
O	5488	11.11	26.61
F	10568	26.10	52.64
Si	2148	3.15	4.29
La	5648	59.64	16.45

the EDX spectrum shows small oxygen composition in the system. The PS is highly reactive and gets oxidized while replacing the PS samples from anodization chamber to vacuum chamber for evaporation. It is difficult to avoid this oxygen. Table 1 shows the atom and weight percentages of various elements in the LaF_3/PS/Si system. The atom percentage ratio of La:F is nearly 1:3 which confirms the stoichiometric nature of the LaF_3 film on PS.

For the as-grown PS samples, single PL peak appeared around 696 nm, which is similar to the reported value[13,14]. A low content of oxygen in the system generally provides the single-peak PL band of PS[15]. Therefore, lower oxygen content was confirmed again from the PL study.

The PL spectra of PS containing three different layers of LaF_3 have been compared with PS having no layer of LaF_3 in Fig. 5. It is clear that PS with thin (e.g., 70-nm thickness) LaF_3 layer enhances the PL intensity but with the increase in the thickness of LaF_3, the PL intensity decreases. And for the sample with LaF_3 of 180±10 nm thickness, the PL intensity of PS decreases even below the PL intensity of the unpassivated PS. The enhancement of the PL intensity can be related to the passivation effect of LaF_3 that prevents oxygen to enter into the PS surface and make covalent bond with Si. Also, there is a possibility of reduction in the nonradiative recombination centers due to the formation of the interface between PS and the nanoparticles of LaF_3, where the nanoparticles of LaF_3 are expected to get embedded into the pores of PS which have similar dimensions.

The decrease in intensity with the increase in LaF_3 thickness may be due to the change in refractive index of LaF_3 layer. The variation of refractive index is induced by the mechanical stress that depends on both the deposition temperature and the film thickness. It is interesting to note that, with increasing thickness, stress changes from high compressive stress at a thickness well below 100 nm to medium tensile at the thickness of

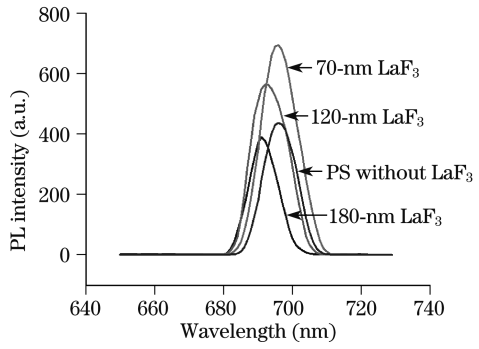

Fig. 5. Comparative PL spectra of PS with and without LaF_3.

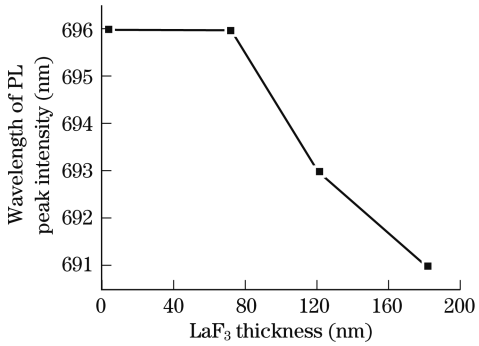

Fig. 6. Small blue-shifts with the LaF_3 thickness.

several hundred nanometers[16]. Evaporated films of higher thickness usually show the columnar grain structure with reduced density, which leads to a lower refractive index and causes a negative inhomogeneity of the refractive index. This is commonly observed within the films of many high-index oxide materials[17,18]. The important thing is the shape of PL response that does not change due to passivation with LaF_3. The full-width at half-maximum (FWHM) of the Gaussian-shaped PL responses of the LaF_3-passivated PS is very narrow (about 12 nm) that implies the homogeneity of the nanocrystal.

The peak wavelengths of the PL spectra of the samples shifted a little towards blue with the increasing thickness of LaF_3, as shown in Fig. 6. This nature of blue-shift has also been reported by Gokarna *et al.* for the PS/CdS and ZnS system[19]. This shift in the wavelength of PL can be attributed to the shrinking of nanocrystallites due to thicker LaF_3 layer[20]. The effect of shrinking of nanocrystallites is not prominent when the thickness of LaF_3 is thin, e.g., 70 nm, that is why we did not observe any blue-shift between unpassivated PS and PS passivated with 70-nm-thick LaF_3.

In conclusion, a LaF_3/PS system has been fabricated and investigated in order to evaluate its possible use in optoelectronics and sensing. LaF_3 grows as the polycrystalline and near stoichiometric thin film on PS. The thickness of the LaF_3 film has an important influence on the PL characteristics of PS. Thinner layer of LaF_3 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 passivation effect of LaF_3 that prevents oxidation of PS. But thicker layer of LaF_3 lowers the PL intensity, which may be due to the degradation of refractive index of the LaF_3 layer induced by the mechanical stress depending on the film thickness. Therefore, it can be concluded that EBE LaF_3 layer can be a simple and low cost solution for the surface passivation of PS. Moreover, the optimum thickness of LaF_3 film on PS could provide the PS an enhanced and stable PL that will enable its use in the fabrication of optical devices like light-emitting diodes (LEDs), lasers, and solar cells.

References

1. A. G. Cullis, L. T. Canham, and P. D. J. Calcott, J. Appl. Phys. **82,** 909 (1997).
2. R. Boukherroub, S. Morin, D. D. M. Wayner, and D. J. Lockwood, Phys. Stat. Sol. (a) **182,** 117 (2000).
3. B. Gelloz, H. Sano, R. Boukherroub, D. D. M. Wayner, D. J. Lockwood, and N. Kashida, Appl. Phys. Lett. **83,** 2342 (2003).
4. T. W. Kang, J. Y. Leem, and T. W. Kim, Microelectron. J. **27,** 423 (1996).
5. S. Ghosh, H. Kim, K. Hong, and C. Lee, Mater. Sci. Eng. B **95,** 171 (2002).
6. A. Missaoui, M. Saadoun, H. Ezzaouia, B. Bessais, T. Boufaden, A. Rebey, and B. Jani, Phys. Stat. Sol. (a) **182,** 189 (2000).
7. H. Park, K. Prabakar, Y. Yoo, S. Hwang, and C. Lee, Mater. Sci. Forum **486–487,** 21 (2005).
8. C. C. Chang and C. H. Lee, Thin Solid Films **379,** 287 (2000).
9. H. Bandarenka, M. Balucani, R. Crescenzi, and A. Ferrari, Super. Microstruct. **44,** 583 (2008).
10. T. Nguyen, P. Joubert, P. Destruel, Ph. Rendu, and M. Lakéhal, Phys. Stat. Sol. (a) **182,** 169 (2000).
11. E. D. Thoma, H. Shields, Y. Zhang, B. C. McCollum, and R. T. Williams, J. Lumin. **71,** 93 (1997).
12. D. R. Lide, (ed.) *Physical Constants of Organic Compounds, in: CRC Handbook of Chemistry and Physics* (87th edn.) (Taylor and Francis, Boca Raton, 2007).
13. H. Li, B. Huang, D. Yi, H. Cui, Y. He, and J. Peng, Chin. Phys. Lett. **19,** 1013 (2002).
14. D. Kim, J. Shim, and N. Cho, Appl. Surf. Sci. **234,** 256 (2004).
15. M. Ohmukai, M. Taniguchi, and Y. Tsutsumi, Mater. Sci. Eng. B **86,** 26 (2001).
16. R. Thielsch, A. Gatto, J. Heber, and N. Kaiser, Thin Solid Films **410,** 86 (2002).
17. J. Borgogno, B. Lazarides, and E. Pelletier, Appl. Opt. **21,** 4020 (1982).
18. A. Tikhonravov, M. Trubetskov, B. Sullivan, and J. Dobrowolski, Appl. Opt. **36,** 7188 (1997).
19. A. Gokarna, S. Bhoraskar, N. Pavaskar, and S. Sathaye, Phys. Stat. Sol. (a) **182,** 175 (2000).
20. L. K. Pan, Y. K. Ee, C. Q. Sun, G. Q. Yu, Q. Y. Zhang, and B. K. Tay, J. Vac. Sci. Technol. B **22,** 583 (2004).