

Investigation on LaF₃-Impregnated Porous Silicon Heterostructure as Potentiometric Sensor for Fluoride Ion in Aqueous Medium

Md. Earul Islam^{1*}, Md. Julkarnain², Jaker Hossain², Abu Bakar Md. Ismail², Md. Hafijur Rahman³

¹Department of Materials Science and Engineering, Rajshahi University, Rajshahi, Bangladesh

²Department of Applied Physics & Electronic Engineering, Rajshahi University, Rajshahi, Bangladesh

³Department of Physics, Pabna University of Science & Technology, Pabna, Bangladesh

*Corresponding author: islam_mse@ru.ac.bd

Received September 03, 2013; Revised September 30, 2013; Accepted October 08, 2013

Abstract Impregnation of pores of porous silicon (PS) by Lanthanum Fluoride (LaF₃) using a novel one-step chemical bath technique, and application of the LaF₃-impregnated porous silicon (PS) structure (LaF₃/PS) as a potentiometric fluoride ion sensor have been investigated in this article. The impregnation of LaF₃ inside the pores of porous silicon was achieved using a chemical bath technique developed by this group. The Scanning Electron Microscopy (SEM) and EDX on the cross-section of LaF₃/PS/Si structure confirmed the LaF₃ film deposition inside the pores of PS. The heterostructure of LaF₃/PS/Si was investigated as fluoride ion (F⁻) sensor in aqueous medium. The high specific area of PS was taken as the key subject to investigate the high fluoride sensitivity of the LaF₃/PS structure in aqueous medium. When experimented with home made fluoride solution having various concentrations the annealed LaF₃/PS/Si structure was found to detect the fluoride ion in aqueous solution. Its response was found linear in the fluoride concentration range of 2.28~4.28 pF. As capacitive sensor the overall fluoride sensitivity was found to be over-Nernstian (400 mV/pF). The experimental results indicate that LaF₃-impregnated porous silicon structure (LaF₃/PS) can be used as a high-sensitive fluoride-ion sensor in aqueous medium.

Keywords: porous silicon, potentiometric sensor, fluoride sensor, capacitive EIPS structure

Cite This Article: Md. Earul Islam, Md. Julkarnain, Jaker Hossain, Abu Bakar Md. Ismail, Md. and Hafijur Rahman, "Investigation on LaF₃-Impregnated Porous Silicon Heterostructure as Potentiometric Sensor for Fluoride Ion in Aqueous Medium." *American Journal of Sensor Technology* 1, no. 1 (2013): 1-4. doi: 10.12691/ajst-1-1-1.

1. Introduction

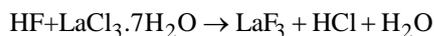
Researchers around the globe are in a quest to find devices for a wide range of applications in several fields that will be highly efficient, compact, low-cost and compatible to existing CMOS fabrication technology. Porous silicon (PS) has attracted an increasing research interest among the candidate materials due to various features like room-temperature photoluminescence and high specific-area. Because of its capability of integrated with standard Si technologies its applications span from biomedicine [1] to biosensing, from photonics [2] to photovoltaic devices [3]. As a substrate material, porous silicon provides many advantages such as large specific surface area, adjustable pore size, miniaturization of capacitive EIS (Electrolyte/Insulator/Semiconductor) sensors etc [4,5]. As the effective sensing area of sensor is large the measuring signal (capacitance value) is also large that enables the miniaturization [5]. PS fabrication is compatible to the conventional semiconductor processing technology for sensor fabrication [6,7] with an added advantage of no need of photolithographic process steps

and additional passivation layers [8]. This makes the sensor fabrication easily and cost-effectively. Although there are significant numbers of studies employing PS as the substrate materials for electrochemical sensing, detection of Fluoride ion (F⁻) in aqueous medium is still to be investigated. Scientific evidence suggests that there are significant risks and negligible benefits from ingesting low levels of fluoride [9]. So, sensing and measurement of fluorine, & fluoride are very important for environmental, biomedical, and Industrial-process monitoring. Electrochemical cells are produced by several companies [10,11] for the detection of fluorine and fluorides. Almost all of them have a liquid electrolyte as the main disadvantage. Recently there are reports on solid state fluorine sensor using LaF₃ thin films as the sensitive layer [12,13,14]. In sensor applications, LaF₃ has been studied as a candidate electrolyte for measuring oxygen gas concentration at room temperature [15,16,17,18]. Most of these studies involved using LaF₃ in polycrystalline form or chunks of single crystal. In those works LaF₃ has been deposited with various deposition techniques, as an epitaxial layer directly, or with additional insulating layer of SiO₂ or Si₃N₄, on semiconductor [19,20,21]. Various sensing mechanism, such as Field-effect transistor [22-28],

Light-addressable potentiometric sensing (LAPS) [29] and capacitive sensor [30], have also investigated for high-sensitive fluoride sensing. But, almost all of them suffered from below-Nernstian sensitivity, i.e. > 59.5 mV/pF. Very recently, use of porous silicon as the substrate for sensors, due to its very high specific surface area, has become the subject of research among the researchers. Zairi et al [31] reported a very high sensitivity of about 177 mV/pNa for Na⁺ ion in aqueous medium with porous structure semiconductor. The sensitivity was higher than Nernstian value, which was reported to be due to the large specific surface area of porous silicon. On the above background of obtaining high sensitivity for different cations sensing using PS, we investigated for the first time the LaF₃/PS heterostructure as a high-sensitive fluoride sensor in the EIPS (Electrolyte-Insulator-Porous-Semiconductor) system. This article first investigates the impregnation of LaF₃ inside the pores of PS, and then explores the possibility of using LaF₃-impregnated PS structure to be used as a fluoride sensor utilizing the very high specific area of PS.

2. Experimental

Porous structure of silicon substrate was formed by electrochemical etching of (111) oriented p-type silicon substrate having a resistivity of 20 Ωcm at a current density of 50 mA/cm² in a HF based solution of ethanol and distilled water at a ratio of 1:2:3 respectively. Porous silicon was produced by maintaining a current density of 50mA/cm² for 30 minutes. The porous silicon substrate was placed inside a home-made chemical-bath for LaF₃ deposition. LaF₃ was deposited using a novel chemical bath deposition technique [31] that allowed deposition of LaF₃ inside the pores of PS. In this technique LaCl₃ solution in hydrochloric acid (HCl) was allowed to react with the hydrofluoric acid (HF) on porous silicon substrate. As a product of the chemical reaction, LaF₃ was produced and the LaF₃ crystal deposited as a layer on PS surface. The basic reaction during LaF₃ deposition is given below:



The whole structure was then annealed at 400°C temperature for 10 minutes in the air. The annealed LaF₃ films show a smoother surface than as-deposited films. The heat energy makes the molecules move and re-crystallize the films that in turn reduces the lattice defects and pores [32]. Finally the heterostructure of LaF₃/PS/Si is given the sensor structure by evaporating aluminum (Al) as the back metal contact. Figure 1 shows the structure of the sensor. This sensor was used as a capacitive-type electrolyte-insulator-semiconductor (EIS) sensor.

Figure 2 shows the experimental setup for capacitance-voltage (C-V) measurement. HP4284A impedance analyzer was employed to measure the C-V characteristics of EIS sensor. By measuring the shift of C-V curve in the potential axis the change in concentration of the fluoride (F⁻) was detected. The LaF₃/PS/Si/Al heterostructure (sensor) was placed in contact with the fluoride buffer solution and for simplicity without using reference electrode the bias was applied through a platinum (Pt) wire. The C-V response was obtained by sweeping the

bias in the range of 3V to -2V that took the heterostructure from accumulation to inversion. A small ac of 15 mV at a frequency of 200 kHz was superimposed with the applied bias. C-V response for various F⁻ concentrations was obtained in the similar fashion.

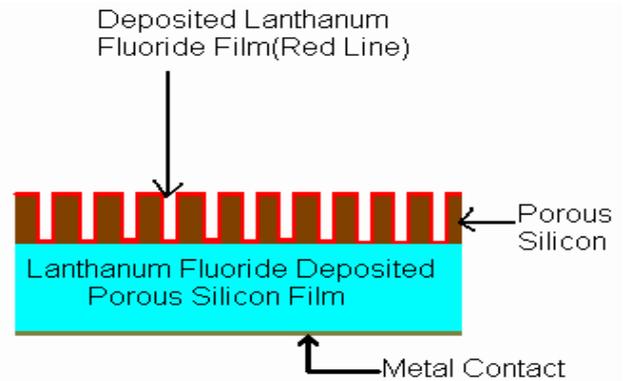


Figure 1. LaF₃ deposited porous silicon heterostructure

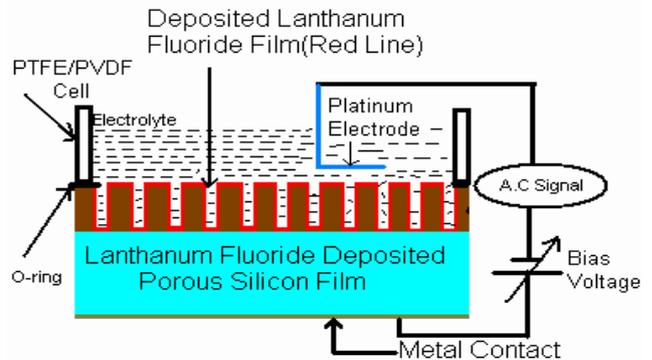
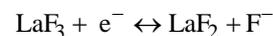


Figure 2. Experimental setup for C-V measurement

The LaF₃ surface responds by interacting with the fluoride ion in solution (electrolyte) and an additional potential develop in the electrolyte, which varies the width of the depletion layer. Depending upon the concentration of fluoride ion (pF) in the electrolyte the resulting surface charge at the interface of the sensing structure affects the depletion layer which also affects the flat band voltage of the sensing system. The basic chemical reaction with the LaF₃ sensing layer with the fluoride ion as follows:



However, from the shift of the C-V curves on the potential axis [32], concentration of fluoride ion was determined. The shift of the C-V curves can be explained by the surface potential variation of the sensor enabled by the surface ionization with F⁻ ion. Home made fluoride solution buffered at constant pH 5.24, with various concentrations, have been experimented with the developed sensor. The standard solution was prepared from Sodium stocks solution. The stock solution was prepared from NaF and buffered at pH 5.24 to avoid unwanted change of the pH of test electrolytes. Buffer solution made of acetic acid, sodium chloride and EDTA, where the EDTA acts as a chelating agent. Again this solution was diluted and made a series of standard solution of different pF. Then different pF (-log [F⁻]) of the aqueous solution of sodium fluoride has been buffered with buffer solution.

3. Result and Discussion

The impregnation the pores of PS by LaF_3 has been confirmed by the SEM on the cross-section of the $\text{LaF}_3/\text{PS}/\text{Si}$ system (Figure 3) that has been annealed at 400°C for 10 min. LaF_3 on PS pores is clearly visible as the white clusters. Several points on the cross-section were selected for EDX to know their corresponding compositions.

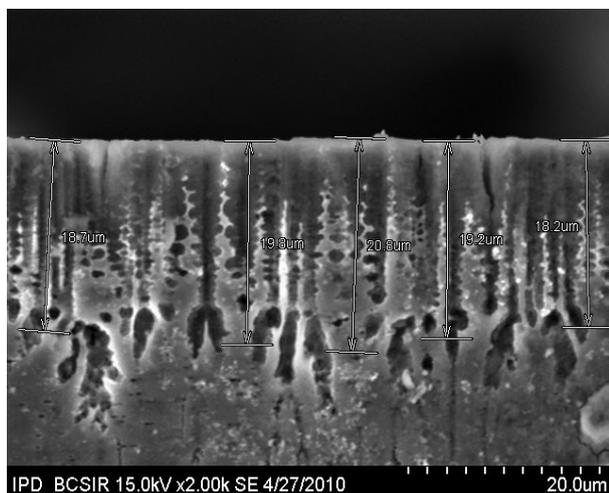


Figure 3. Cross-sectional SEM image of the LaF_3/PS heterostructure

The EDX spectrum of a point on the cross-section is shown in Figure 4. The ratio of the La and F atom was 1:15 at that point. For a stoichiometric LaF_3 deposition the ratio should be 1:3. In our case the fluorine source was HF and why the stoichiometry of LaF_3 was not good. If TiF_4 or TaF_5 type of electrolyte could be used we could have received better stoichiometry of LaF_3 .

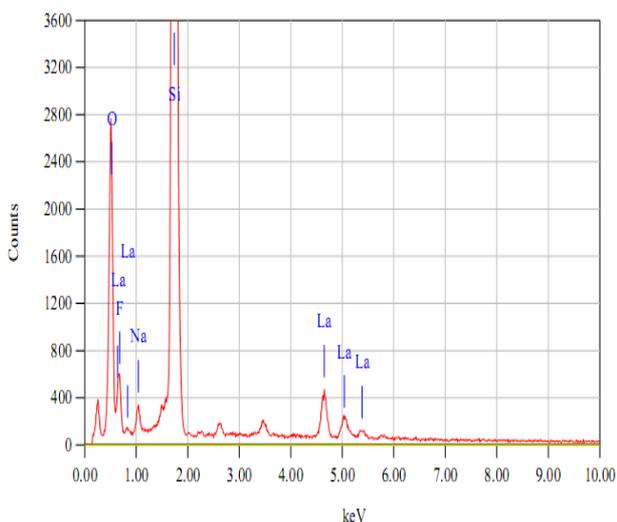


Figure 4. EDX spectra on the cross-section of the LaF_3/PS heterostructure

Sensors with two conditions, namely, as-deposited (without annealing) and, annealed at 400°C , were investigated. As the as-deposited sensor shows hardly any shift in potential axis with change in fluoride ion concentration [35], from now on only the annealed structure will be investigated as the sensor. The response for a particular solution is obtained by plotting the capacitance for the corresponding bias. The typical

response of the sensor for a pF 2.28~4.28 solutions is shown in Figure 5. As shown in Figure 5, the capacitance for sensors start decreasing when the depletion region is created in the interface of LaF_3 and porous-Si by the applied bias and the surface potential at the $\text{LaF}_3/\text{electrolyte}$ interface which corresponds to the Nernstian voltage of LaF_3 for pF solutions. The minimum level of the capacitance was observed at highly depleted condition at a bias of -1 V. The change in the concentration (pF) of the fluoride solution is measured by determining the shift in the C-V curve on the potential axis (bias) from any reference pF value.

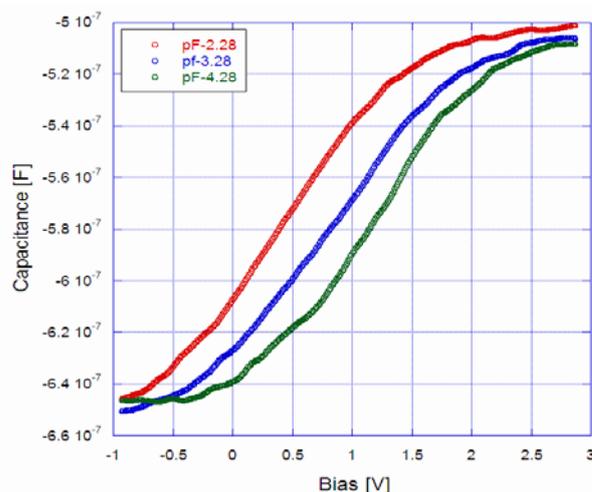


Figure 5. C-V response of the sensor for different pF solution

The potential change for different pF found from the zero crossing point in the second derivative of C-V response signal. Figure 6 shows the second derivative of signal of 4.28 pF solution.

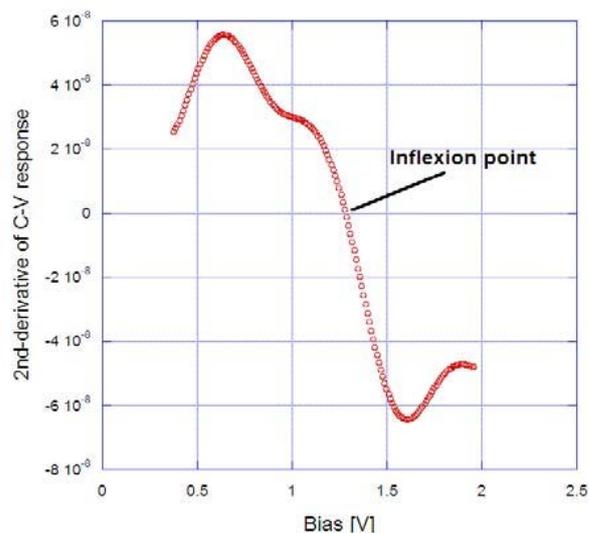


Figure 6. Second derivative of C-V response showing the inflexion point

After calculating the inflexion potentials for all the fluoride concentrations (pFs) the calibration curve was obtained, which is shown in Figure 7. From the calibration curve the average sensitivity [5,14] of sensor was found to be 400 mV/pF. This over Nernstian behavior of the sensor is believed to be due to the enlargement of the active area of PS and excellent adhesion between sensing fluorides and the surface of the porous silicon [33,34].

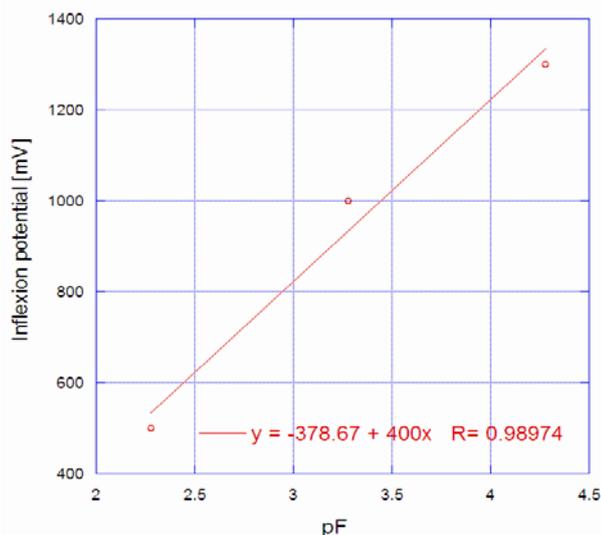


Figure 7. Sensitivity curve of the sensor for different pF solution

4. Conclusion

A novel chemical bath technique was used to impregnate LaF_3 inside the pores of porous silicon. The resulting heterostructure of $\text{LaF}_3/\text{PS}/\text{Si}$ was investigated as a high-sensitive fluoride ion sensor in aqueous medium exploiting the high specific-area of porous silicon. Use of chemical route facilitated the deposition of LaF_3 inside the pores of porous silicon with out any oxide layer. When experimented as a potentiometric capacitive sensor in electrolyte-insulator-semiconductor (EIS) principle with home-made fluoride solution of various concentrations the sensor response was found linear in the detection range of pF-2.28~pF4.28. The fluoride sensitivity was found to be 400 mV/pF, which was much higher than the Nernstian value (~59 mV/pF). This over-Nernstian sensitivity towards fluoride-ion concentration most probably was due to the large specific active area of the porous silicon. Experimental results indicate a possibility of $\text{LaF}_3/\text{PS}/\text{Si}$ heterostructure to be used as a high sensitive fluoride ion sensor in aqueous medium.

References

- [1] Anglin, E. J., L. Cheng, W. R. Freeman and M. J. Sailor (2008). *Advanced Drug Delivery Reviews*, Vol.60, pp. 1266-1277.
- [2] Huy, B., P. V. Hoi, P. H. Khoi, D. K. Van, P. T. Binh and T. T. Cham (2009). *Journal of Physics: Conference Series*, Vol.187, pp. Article number 012033.
- [3] Xiong, Z., F. Zhao, J. Yang and X. Hu, *Applied Physics Letters*, 96, 181903 (2010).
- [4] Lehmann, V.; Hönlein, W.; Reisinger, H.; Spitzer, A.; Wendt, H.; Willer, J. A novel capacitor technology based on porous silicon. *Thin Solid Films*, 276, 138 (1996).
- [5] Schöning, M. J.; Kurowski, A.; Thust, M.; Kordos, P.; Schultze, J. W.; Lüth, H. *Sens. Act. B* 64, 59 (2000).
- [6] Barret, S.; Gaspard, F.; Herino, R.; Ligeon, M.; Muller, F.; Ronga, I. Porous silicon as a material in microsensor technology. *Sens. Act. A*, 33, 19 (1992).
- [7] Smith, R. L.; Scott, D. C. An integrated sensor for electrochemical measurements. *IEEE Trans. Biomed. Eng.* 33, 83 (1986).
- [8] Bergveld, P. Development of an ion-sensitive solid-state device for neurophysiological measurements. *IEEE Trans. Biomed. Eng.* BME-17, 70 (1970).
- [9] M. Diesendorf, J Colquhoun, B J Spittle, D N Everingham and F W Clutterbuc, *Fluoride*, 30, 179 (1997).
- [10] T. Gotjamanos, *Aust. Dent. J.* 42, 166 (1997).
- [11] T. Ichichi, M. Shoichi, M. Ishizuka, *Japanese Patent* 07, 55, 768, Riken Keiki (1995).
- [12] Wei G, Yin J, Ma X, Yu S, Wei D, Du Y, *Anal Chim Acta*, 703, 219 (2011).
- [13] S. Guha and S. Saha, *J. Am. Chem. Soc.* 132, 17674 (2010).
- [14] A. B. M. Ismail, K. Furuichi, T. Yoshinobu and H. Iwasaki, *Sens. Actuat. B*, 86, 94 (2002).
- [15] T. Katsube, M. Hara, I. Serizawa, *Jpn. J. Appl. Phys.* 29, L392 (1990).
- [16] J. Lukaszewicz, N. Miura, N. Yamazoe, *Sens. Actuat.* 1, 195 (1990).
- [17] N. Miura, J. Hisamoto, N. Yamazoe, S. Kuwata, J. Salardenne, *Sens. Actuat.* 16, 301 (1989).
- [18] S. Harke, H.D. Wiemhöfer, W. Göpel, *Sens. Actuat. B*, 1, 188 (1990).
- [19] S. Sinharoy, R. A. Hoffman, J. H. Rieger, W. J. Takei, and R. F. C. Farrow, *J. Vac. Sci. Technol. B*, 3, 722 (1985).
- [20] S. Sinharoy, R. A. Hoffman, A. Rohatgi, R. F. C. Farrow, and J. H. Rieger, *J. Appl. Phys.* 59, 273 (1986).
- [21] R. Strumpler, D. Guggi, H. Luth, *Thin Sol. Films*, 198, 221 (1991).
- [22] W. Moritz, I. Meierhofer and L. Muller, *Sens. Actuat.* 15, 211 (1988).
- [23] R. Hintsche et al, *Anal. Lett.* 22, 2175 (1989).
- [24] R. Hintsche et al, *Biosens. Bioelec.* 5, 327 (1990).
- [25] R. Hintsche, I. Dransfeld, *Anal. Lett.* 23, 451 (1990).
- [26] Dransfeld et al, *Anal. Chem.* 333, 23 (1988).
- [27] Z. M. Baccar, N. Jaffrezic-Renault, C. Martelet, *J. Mater. Sci.* 32, 4221 (1997).
- [28] T. Gabusjan, L. Bartholomäus, W. Moritz, *Sens. Mater*, 5, 263 (1998).
- [29] A. B. M. Ismail, R. Islam, K. Furuichi, T. Yoshinobu, H. Iwasaki, *IJUM Eng. J.* 6, 37 (2005).
- [30] A. A. Mortuza1, M. H. Rahman, S. S. Mou, M. Julkernain, A. B. M. Ismail, *Int. J. Mat. Chem*, 111 (2012).
- [31] S. Zairi, C. Martelet, N. Jaffrezic-Renault, R. M'gaieth, H. Maaref, R. Lamartine, *Thin sol. Film*, 383, 325 (2001).
- [32] R. C. Sikder, S. S. Mou, A. Rahman and A. B. M. Ismail, *Sens. Act. B*, 135, 488 (2009).
- [33] Andrea Edit Pap, <http://herkules oulu.fi/isbn9514277759/>
- [34] R. Sabet-Dariani, N. S. McAlpine, and D. Haneman, *J. Appl. Phy.* 75, 8008 (1994).
- [35] A. B. M. Ismail, K. Furuichi, T. Yoshinobu, and H. Iwasaki, *Sens. Actuat. B*, 71, 169 (2000).