INVESTIGATION ON LAF$_3$/Si STRUCTURE AS LIGHT-ADDRESSABLE POTENTIOMETRIC FLUORIDE (F^-) SENSOR

ABU BAKAR MD. ISMAIL[1,2], REZAUL ISLAM[1], KOJI FURUICHI[2], TATSUO YOSHINOBU[2], HIROSHI IWASAKI[2]

[1]Department of Applied Physics and Electronics, Rajshahi University

Rajshahi 6205, Bangladesh. Tel: 880-721-750041/4101, Fax: 880-721-750064,

E-mail: ismail@ru.ac.bd; and ismail_abm@lycos.com

[2]The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan. 8404

E-mail: iwasaki@sanken.osaka-u.ac.jp

Abstract: In this article LaF_3 films in LaF_3/Si structure have been investigated for the measurement of fluoride ions in aqueous solution with higher accuracy using light-addressable potentiometric sensing technique. LaF_3 films were directly grown on Si by vacuum evaporation. The effects of LaF_3-thickness and annealing on the fluoride-sensitivity of the LaF_3/Si structures have been studied. Accordingly four different LaF_3/Si structures with various thickness of LaF_3 (5/50/150nm) layer were fabricated. The structures are annealed at 400ºC for 10 minutes. The un-annealed LaF_3/Si structures show very poor fluoride sensitivity. As predicted in the theoretical study structures with thinner LaF_3 offer better steepness of the photocurrent characteristics that indicates better accuracy in fluoride concentration measurement. Among the annealed structures, the one prepared with 150nm LaF_3 layer shows the best fluoride sensitivity of ≈ 54.5mV/pF in the range of pF1-pF4. Experimental results show a good promise for LaF_3/Si structure as a light-addressable potentiometric sensor that can be used for the sensing and imaging the distribution of fluoride ion in aqueous medium with higher accuracy.

***Keywords**: Light-addressable potentiometric sensor (LAPS), Fluoride sensor, Capacitive EIS structure*

1. INTRODUCTION

In recent years, new scientific evidence has emerged which suggests that there are significant risks and negligible benefits from ingesting low levels of fluoride [1]. Fluoridation of water supplies is harmful to bone, while providing negligible benefits when swallowed. Therefore, monitoring of fluoride has become very important for the environmental and the industrial processes. Generally detection of fluorine and fluorides are done by Electrochemical cells [2]. Almost all of them have a liquid electrolyte, which is considered as their main disadvantage. Recently there are reports on the ionic conductor LaF_3 thin-film as the sensitive layer in solidstate sensors for both fluorine and oxygen sensing. Researchers have investigated LaF_3 in details for its various attributes such as its crystal structure, ionic conductivity and dielectric properties.

As a candidate electrolyte for measuring oxygen gas concentration at room temperature use of LaF3 has been studied thoroughly [3-9] by some researchers. Most of these studies involved the LaF_3 in polycrystalline form or chunks of single crystal. In those works LaF3 have been deposited with various deposition techniques as an epitaxial layer directly, or with additional insulating layer of SiO_2 and/or $Si3N_4$, on semiconductor. The interface between epitaxially grown LaF_3 on silicon or gallium arsenide [10-12] has also been studied to obtain a heterostructure of low density of surface states. Development of fluoride sensitive field-effect transistors (pF-FET) have been carried out by Moritz [13], Hentsche et al. [14]. Baccar et al. [15] also investigated ion sensitive field-effect transistor (ISFET) and electrolyte-oxide-semiconductor (EOS) structure with a fluoride ion sensitive membrane obtained by fluoride and lanthanum ion implantation into the silica insulator layer. An overview of the above reports suggests that epitaxially grown LaF_3 on Si <100> would give an interesting structure to be used for fluoride sensing. Apart from the choice of sensor materials, the choice of sensing technique is also important. Recently sensors based on light-addressable potentiometric sensing (LAPS technique has become popular [16-18] due to some of its advantages, such as selection of measurement point by a scanning light beam and spatial resolution. In our previous work [19] we first reported a Fluoride sensor using Si/LaF_3 structure as light-addressable potentiometric sensor (LAPS). For potentiometric sensors high precision measurement is necessary since 1 mV in the potential shift corresponds to an error in concentration of 4% (exchange of one electron) [20]. Therefore the steepness of the LAPS IV characteristics is of great importance for achieving accurate measurements. This article presents the investigation on vacuum evaporated LaF_3 on Si in a heterostructure of LaF_3/Si/Au to be a high-accuracy fluoride-sensitive LAPS devices. The possibility of obtaining high accuracy in fluoride sensing is first theoretically studied, and then experimentally it is verified.

2. SENSOR FABRICATION AND EXPERIMENTAL SETUP

The sensor chips were obtained from small pieces of silicon cut from an n-type Silicon wafer having a diameter of 8 cm, resistivity ρ of 1-10 Ω-cm and surface of (100) orientation. The back surface (unpolished) of silicon chips was first coated with AuSb (99.5%-Au and 0.5%-Sb) to establish the back metal contact of the sensor. The above-mentioned wafer was first degreased ultrasonically in acetone and deionized water. The pieces were briefly dipped in very dilute (2 %) HF solution to remove the native oxide just before insertion into the evaporation chamber. The LaF3 films were deposited in a home-assembled vacuum-coating unit. LaF3 anhydrous 99.99% purity was purchased from Kishida Chemical Co. Ltd., Japan, and was used without further purification. The vacuum pressure was maintained in the range of 10-8 Torr. The deposition rate was 5 nm/min. In this way, 5 nm (Sensor 2), 50 nm(Sensor 3), 150 nm (Sensor 4) -thick LaF_3 layers were deposited on the bulk Si. The thicknesses were monitored in-situ as well as confirmed by ellipsometric measurements. The sensors (2, 3 and 4) thus constructed were annealed at 400ºC for 10 min.

3. THEORETICAL CONSIDERATION

Theoretically it appears that the optimization of heterostructure of LaF_3/Si to be used as a LAPS might provide the steeper photocurrent response and thereby provide better accuracy in the measurement of Fluoride concentration. The electrical equivalent circuit of the LaF3/Si structure to be used as LAPS can be given [21] as shown in Fig. 1.

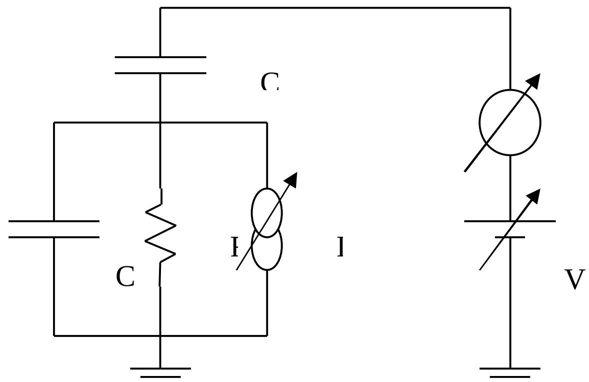


Fig. 1: AC equivalent circuit of LAPS device.

The measured current is given by

$$I = I_p \frac{j\omega C_i R}{1 + j\omega R(C_i + C_d)} \tag{1}$$

Where, I_p = Current due to Light induced minority carriers

I = Measured photocurrent

C_d = Depletion capacitance

C_i = Insulator capacitance

R = Depletion resistance

ω = Angular frequency of AC photocurrent

The term $[2\pi R(C_i + C_d)]^{-1}$ is defined as the cutoff frequency for the LAPS. The measured current, at a frequency below the cutoff, is given by

$$I \approx j\omega C_i R I_p \tag{2}$$

Above the cutoff frequency the measured current is given by

$$I = \frac{C_i}{C_i + C_d} I_p \tag{3}$$

Equations (2) and (3) show that, at a frequency below or above the cutoff frequency, the measured current can be increased by increasing the insulator capacitance C_i ($\propto 1/d$), and hence decreasing the thickness (d) of the insulating layer. Conventionally the insulating layer of LAPS is a combination SiO_2 and $Si3N_4$, as such the insulator capacitance of

$$C_{i(LaF3)} >> C_{i(SiO2+Si3N4)}$$

Therefore, using very thin LaF_3 layer as the insulating layer in LAPS the measured photocurrent and hence the steepness of the I-V response can be increased. The steepness of the I-V characteristics is of great importance for achieving better resolution. The steepness of the photocurrent response is defined as the change of photocurrent for the unit change in surface potential, at the linear region of the photocurrent response characteristics around the inflexion point of the I-V characteristics.

4. RESULTS AND DISCUSSION

For the investigation of LaF_3 material as the fluoride ion sensitive material in the LAPS, sensors with two conditions, namely, as deposited (without annealing, Sensor 1) and, annealed at 400°C (Sensor 2, 3 and 4), were studied. The test solutions used in the characterization were prepared in the laboratory. The composition of the solutions was 2% tris (hydroxymethyl)-aminomethane solutions in distilled water, at a fixed pH value of 7.2. Constant ionic strength was maintained at 0.4 M of KNO_3. Analytical grade KF was added to the solution in a concentration range of 10^{-1}M to 10^{-7}M to obtain the experimenting solutions having pF values from 1 to 7. As shown in Fig 2, the response for a particular solution is obtained by plotting the photocurrent for the corresponding bias. The typical response of the sensors for a pF2 solution is shown in Fig. 3.

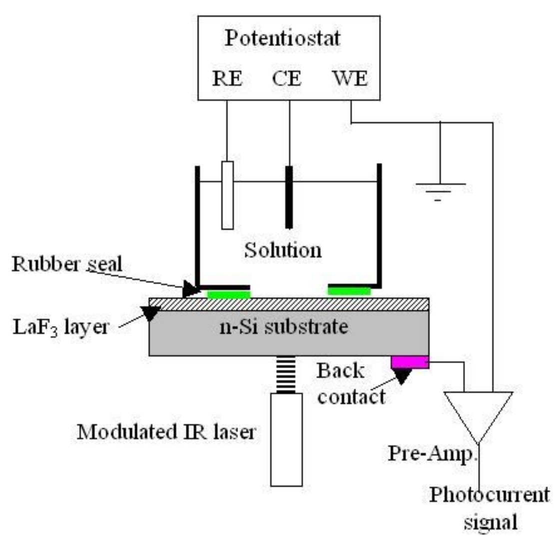


Fig. 2: Experimental set-up for the LAPS measurement.

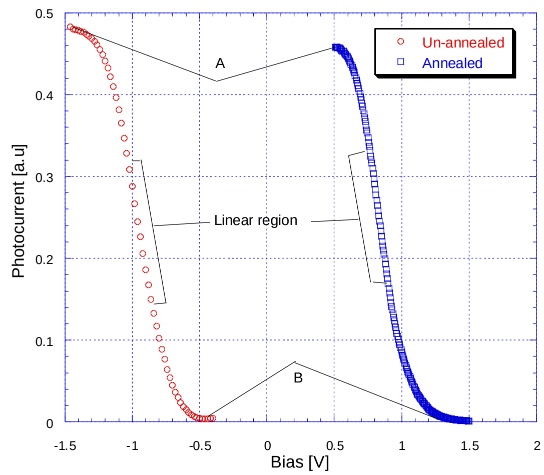


Fig. 3: Typical LAPS response of the 50nm-LaF_3/Si structure for pF4 solution.

As shown in Fig. 3, the photocurrent for the LaF_3/Si structures start flowing when the depletion region is created in the Si by the applied bias plus the surface potential at the insulator/electrolyte interface which corresponds to the Nernstian voltage of LaF_3 for pF4 solution. The saturation level of the photocurrent is observed at the highly depleted (inverted) condition. As the bias is further decreased towards less positive values the photocurrent starts decreasing and then becomes nearly constant. The responses of various thickness LaF_3/Si structures used as the Fluoride-LAPS are compared for a particular solution (pF4) and are shown in Fig. 4. As the theory predicts the amplitude of the photocurrent as well as the steepness of the response characteristics for the LaF_3-based LAPS depends on the LaF_3 thickness.

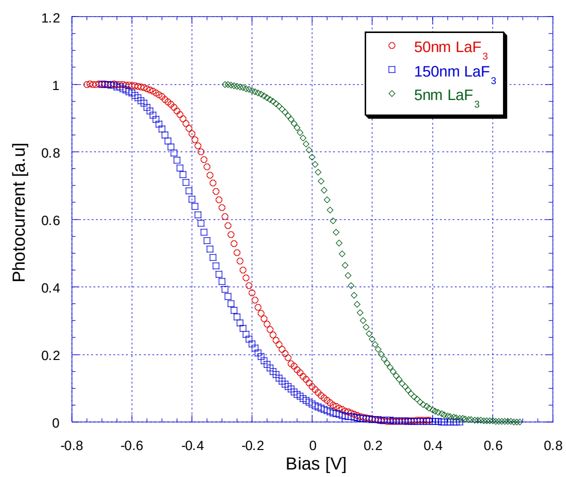


Fig. 4: Photocurrent response of annealed-LaF_3/Si structures for various thickness of LaF_3.

Figure 5 shows the linear portion of the photocurrent characteristics around the inflexion points. This plot is used to calculate the steepness of the photocurrent characteristics. The steepness is calculated as the change of photocurrent for unit change in surface potential. For our experimental setup, since we used a preamplifier to convert the photocurrent into voltage by a factor of 106, the Steepness of the photocurrent response is defined as,

$$Steepness = \frac{Change\ in\ photocurrent\ (A)\ x10^{6}\ (V/A)}{Change\ in\ Bias\ (V)}$$

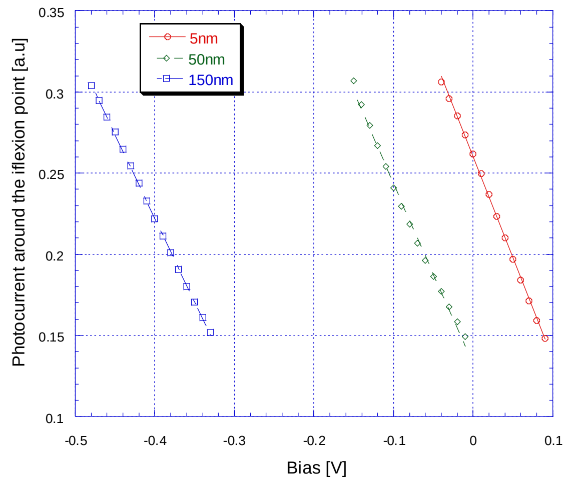


Fig. 5. Linear portion around the inflexion point of the photocurrent characteristics of various thickness annealed structures.

Figure 6 shows the calculated-stpeeness versus the LaF_3 thickness for the annealed structures corresponding to the pF4 solution. The steepness of the annealed structures was always higher than the un-annealed structures. This is evident from the Fig. 3. Thus, we will focus on the behavior of annealed structures. As predicted theoretically, the steepness of the photocurrent characteristics was inversely proportional to the thickness of the LaF3 layer on Si.

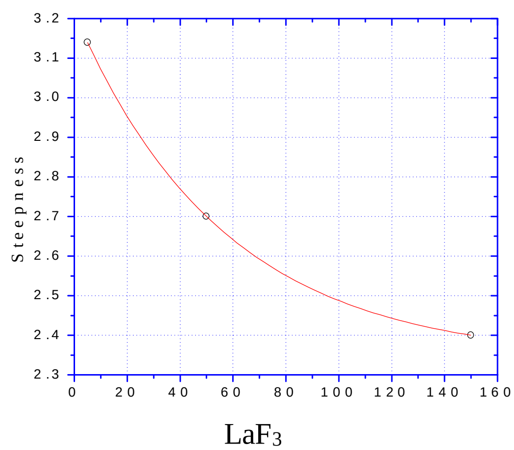
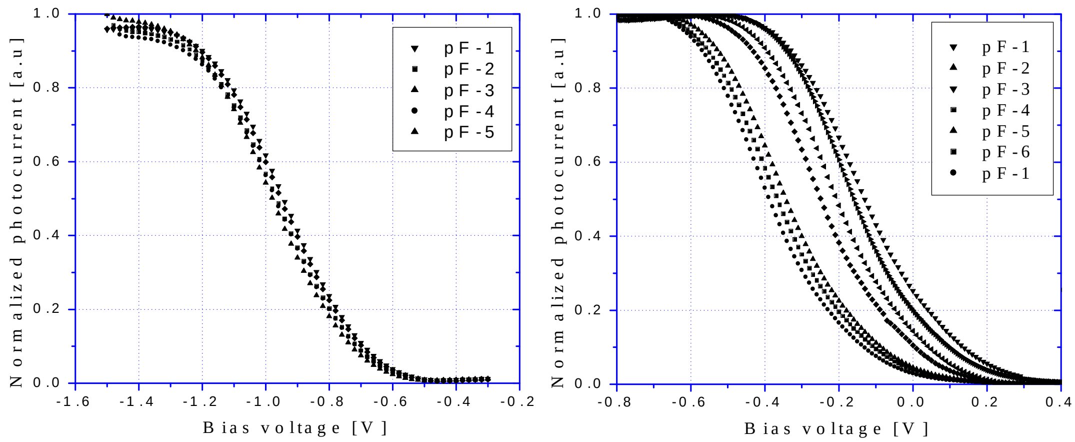


Fig. 6. Steepness versus LaF_3 thickness for the annealed-structures.

Figure 7 shows the typical photocurrent response of the annealed structures for varied concentration fluoride solutions in the range of pF1 to pF7. Here, each I-V curve is normalized at its peak value. The un-annealed (as-deposited) sensor showed indistinguishable or very low fluoride sensitivity. Therefore, the response of the annealed sensors will be discussed further.



a) Un-annealed LaF3/Si structure b) Annealed LaF_3/Si structure

Fig. 7. Photocurrent response for varied concentration of Fluoride solution.

As can be seen in Fig. 7(b), the photocurrent response for the pF5, pF6 and pF7 solution appears to be overlapping which suggests a loss in Fluoride sensitivity when the sensor is subjected to pF solution beyond pF4. The inflexion points for the photocurrent responses of various pF solutions are found by equating the second derivative of the response for each buffer to zero, and are plotted as shown in Fig. 8 for the annealed structures. The un-annealed structures did not show distinguishable inflexion voltages for various fluoride concentrations and are not plotted for simplicity in Fig. 8. The 50nm-LaF_3/Si structure shows quite linear response for pF1 to pF5 whereas 5 nm-LaF_3/Si and 150 nm-LaF_3/Si structures show linear responses for pF1 to pF4 value of the solution.

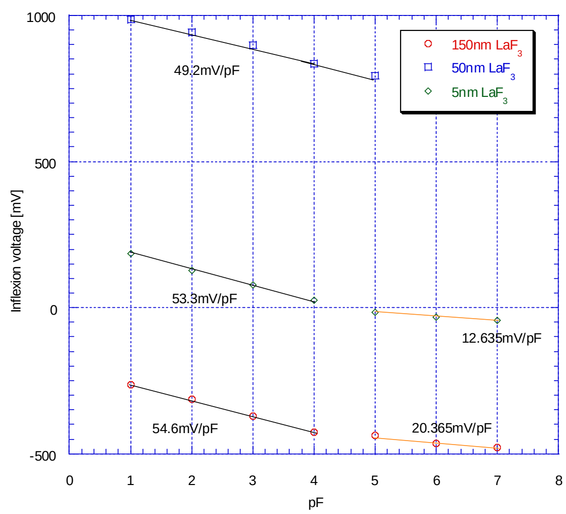


Fig. 8. Thickness dependency of the inflexion potentials.

Figure 9 shows the plot of the fluoride sensitivity against the thickness of the sensor. We didn't find any ordered relationship between thickness of the LaF_3 layer and Fluoride sensitivity. This is may be due to the fact that the fluoride sensitivity of LaF_3 layer depends on the number of surface sites, which binds the fluoride ion and does not depend on the thickness of the layer. The minimum average sensitivity of 49.2 mV/pF was observed in this experiment with the 5 nm-LaF_3/Si. The highest sensitivity of 54.6 mV/pF was obtained with 150nm-LaF_3/Si. The minimum average sensitivity of the sensors was more than that obtained by Baccar *et al*. [15] for their sensor prepared with ion implantation technique (44 mV/pF). The detection limit for 5 nm-LaF_3/Si structure was also higher than that obtained by Baccar et al (pF 2 - 4). But the detection limit of 50 nm-LaF_3/Si and 150 nm-LaF_3/Si structures is quite similar to that of what *Baccar et a.l* obtained.

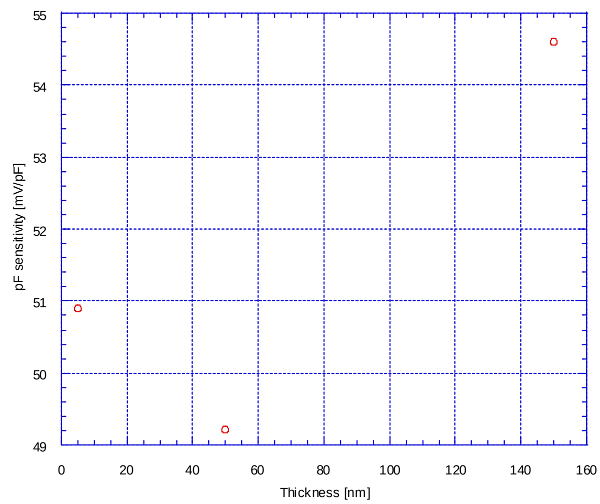


Fig. 9. Thickness versus sensitivity plot.

5. CONCLUSION

Vacuum-evaporated LaF_3 layer as fluoride-sensitive material in a heterostructure of Si/LaF3 as a sensor in a LAPS device has been investigated for obtaining fluoride measurement with higher accuracy. The sensor those were annealed at 400°C after the deposition of LaF_3, show good average fluoride sensitivity in their first use. But, the sensor not annealed hardly shows fluoride sensitivity. The thinner LaF_3 layer provides better steepness of the photocurrent response hence better accuracy of Fluoride measurement. Observing the performance of this simple structure, it can be concluded that very thin layer of epitaxial-LaF_3 on Si heterostructure can be used for fluoride ion measurement with higher accuracy as an LAPS device.

REFERENCES

[1] M. Diesendorf, J Colquhoun, B J Spittle, D N Everingham and F W Clutterbuck, "New evidence on fluoridation," Fluoride, vol. 30, no. 3, pp. 179-185, August 1997.

[2] T. Ichichi, M. Shoichi, M. Ishizuka (Riken Keiki), "Potentiostatic electrolytic acid gas sensor," Japanese Patent 07, 55,768, March 3, 1995.

[3] T. Katsube, M. Hara, and I. Serizawa, " MOS-type micro-oxygen sensor using LaF3 workable at room temperature," Jap. J. Appl. Phys., Vol. 29, no. 8, pp. L-1392-1395, August 1990.

[4] N. Yamazoe and N. Miura, “Solid-state electrochemical oxygen sensors for operation at room temperature,” Trends Anal. Chem., vol. 9, no. 5, pp. 170-175, May 1990.

[5] J. Lukaszewicz , N. Miura and N. Yamazoe, “A LaF3-based oxygen sensor with perovskite-type oxide electrode operative at room temperature,” Sensors & Actuators B, vol. 1, no. 1-6, pp. 195-198, January 1990.

[6] Yamazoe N. et al., “Potentiometric solid-state oxygen sensor using lanthanum fluoride operative at room temperature,” Sensors & Actuators, vol. 12, no. 4, pp. 415-423, November –December 1987.

[7] N. Miura, J. Hisamoto, N. Yamazoe, S. Kuwata, " LaF3 sputtered film sensor for detecting oxyzen at room temperature," Appl. Surface Sci., vol. 33-34, pp. 1253-1259, September 1988.

[8] N. Miura, J. Hisamoto, N. Yamazoe, S. Kuwata, and J. Salardenne, " Solid-state oxygen sensor using sputtered LaF3 film," Sensors & Actuators, vol. 16, no. 4, pp. 301-310, April 1989.

[9] S. Harke, H. D. Wiemhöfer and W. Göpel, " Investigation of electrodes for oxygen sensor based on lanthanum trifluoride as solid electrolyte," Sensors & Actuators B, vol. 1, no. 1-6, pp. 188-194, January 1990.

[10] S. Sinharoy, R. A. Hoffman, J. H. Rieger, W. J. Takei, and R. F. C. Farrow, “Epitaxial growth of lanthanide trifluorides by MBE,” J. Vac. Sci. Technol., vol. 3, no. 2, pp. 722 – 723, March 1985.

[11] S. Sinharoy, R. A. Hoffman, A. Rohatgi, R. F. C. Farrow, J. H. Rieger, " Epitaxial growth of LaF3 on GaAs(111)," J. Appl. Phys. vol. 59, no. 1, pp. 273-275, January 1986.

[12] R. Strümpler, D. Guggi and H. Lüth, “The structure of thin epitaxial LaF3 films on Si(111),” Thin Solid Films, vol. 198, no. 1-2, pp. 221-232, March 1991.

[13] W. Moritz, I. Meierhofer and L. Müller, “Fluoride-sensitive membrane for ISFETs,” Sensors & Actuators, vol. 15, no. 3, pp. 211-219, November 1988.

[14] R. Hintsche, I. Dransfeld and F. SchellerM. T. Pham, W. Hoffmann and J. HuellerW. Moritz, “Integrated differential enzyme sensors using hydrogen and fluoride ion sensitive multigate FETs,” Biosensors Bioelectron.,vol. 5, no. 4, pp. 327-334, 1990.

[15] Z. M. Baccar, N. Jaffrezic-Renault, C. Martelet, " New fluoride-sensitive membranes prepared through an ion implantation process," Jour. Mater. Sci., vol. 32, no. 16, pp. 4221-4225, January 1997.

[16] M. Nakao, T. Yoshinobu, and H. Iwasaki, " Scanning-laser-beam semiconductor pH-imaging sensor", Sensors & Actuators B, vol. 20, no. 2-3, pp 119-123, June 1994.

[17] G. Gehring, D. L. Patterson, and S. Tu, " Use of a Light-Addressable Potentiometric Sensor for the Detection of Escherichia coliO157:H7," Anal. Biochem., vol. 258, no. 2, pp. 293-298, May 1998.

[18] A. B. M. Ismail, T. Harada, T. Yoshinobu, H. Iwasaki, M. J. Schoening, and H. Lueth, " Investigation of pulsed laser-deposited Al2O3 as a high pH sensitive layer for LAPS-based biosensing applications," Sensors and Actuators B, vol. 71, no. 3, pp. 169-172, December 2000.

[19] A. B. M. Ismail, K.Furuichi, T. Yoshinobu and H. Iwasaki, " Light-addressable potentiometric Fluoride(F-) sensor," Sensors and Actuators B, vol. 86, no. 1, pp. 94-97, August 2002.

[20] T. Gabusjan, L. Bartholomäus, W. Moritz, " Improved ion-conducting layer replacing the insulator in a capacitive chemical semiconductor sensor," Sensors Materials, 10(5), 263-273, (1998).