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Performance of In_2TiO_5 Based Bio-sensor Treated by CF_4 Plasma

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Abstract- In this study, the electrolyte-insulator-semiconductor biosensor device using In_2TiO_5 sensing membrane and combined with CF_4 plasma treatment has been investigated. It can be found that the better sensing characteristics such as higher sensitivity (59.64 mV/pH) after plasma treatment at 60sec, including lower hysteresis voltage and higher linearity about 99.68%.

I. Introduction

Electrolyte-Insulator-Semiconductor (EIS) biosensors are one of the most promising candidates for bio-analyte sensing due to its excellent transducers for sensing biochemical reactions owing to their small size, fast response, and reliability. properties. Recently, researchers have focused on Ti-doped Indium oxide (Ti-doped In_2O_3) thin films owing significant attention as a sensing membrane because it has higher mobility (160 $cm^2/(V\cdot s)$) [1], higher melting point (1910 ℃), larger band gap (3.5–3.7 eV) [2], According to the literature, In_2TiO_5 films can easily be reduced to create an oxygen deficiency, where insufficient oxygen atoms are contained in the crystal structure. As a potential solution, CF_4 plasma treatment of the In_2TiO_5 film can enhance the In-Ti-O bonding as well as increase the sensing performance. In this work, we used post-deposition CF_4 plasma treatment on In_2TiO_5 thin-films to improve their physical and biosensing characteristics.

II. Experiment

The EIS structures of a high-k In_2TiO_5 sensing membrane were fabricated on 4-inch n-type (100) Si wafers. A 50 nm thick SiO_2 substrate was thermally oxidized on the silicon wafer. A 50 nm In_2O_3 film was deposited on the Si substrate by using sputtering system. The indium target is used for deposition. An another Ti doped In_2O_3 sample is prepared using co-sputter technique. Subsequently, samples were plasma treatment in CF_4 ambient for 15 sec, 30 sec and 60 sec. After that, the back-side contact of the Si wafer was deposited by Al film with 300nm-thick. The sensing area of the deposited In_2TiO_5 films was defined by an automatic robot dispenser with an adhesive silicone gel. Finally, the samples were placed on the copper lines of printed circuit board (PCB) by pasting with silver gel. Epoxy package was used to separate the EIS structure and the copper line (Fig.1)

III. Results and Discussion

Fig. 2(a)-(d) shows the C-V curves In_2TiO_5 and sensing membrane by CF_4 plasma treatment (15 sec to 60sec) in buffer solution with various pH values. The sample of In_2TiO_5 and treated in the plasma of 60sec possessed the highest sensitivity. It showed that the capacitance value of the EIS device with CF_4 plasma treated at 30sec is smaller than that of treated at 60 sec indicating the formation of a thicker amorphous In-Ti silicate layer at the In_2TiO_5/Si interface. Therefore, the pH sensing membrane with a proper CF_4 plasma treatment at 60 sec can obtain an excellent linearity and high sensitivity. Fig. 3(a)-(c) shows hysteresis voltage and drift rate under different CF_4 plasma treatment time conditions, and illustrates the lowest hysteresis voltage of 2.72 mV and the lowest drift rate of 0.42 mV/hr for the 60 seconds plasma treated sample. Proper plasma treatment can repair bond connections and defects in the In_2TiO_5 film by fluorine incorporation.

Fig. 4 shows the XRD spectra of high-k In_2TiO_5 film before and after CF_4 plasma treatment samples. It can be seen that the CF_4 plasma treatment can induce crystallization in high-k sensing membrane, and the sample with CF_4 plasma treatment at 60 sec exhibited a stronger peak intensity in In_2TiO_5 (222). Besides, in order to investigate the composition and chemical behaviors of high-k In_2TiO_5 film, Fig. 5(a)-(b) shows the O 1s and In 3d XPS spectra of In_2TiO_5 sensing membrane. In addition, the In_2TiO_5 plasma treatment at 60 sec film can be seen the In 3d peak located at 452.26 eV and 444.65 eV. The O 1s spectra of In_2TiO_5 film exhibited a smaller In-Ti silicate peak (531.8 eV) when the sensing membrane is treated by plasma for 60 seconds. This result indicates that the In_2TiO_5 with CF_4 plasma at 60 seconds could reduce SiO_2 and silicate formation.

Fig. 6(a)-(b) shows AFM images of the In_2TiO_5 sensing membrane for the as-deposited and CF_4 plasma treatment at 60 sec samples. The root mean square (rms) values of the above samples were 0.62 nm, and 2.92 nm, respectively. Because of interior grain size and structure, which became stronger and larger as CF_4 plasma treatment time increased.

Fig. 7 shows the urea concentration controlled in a range between 5mM, and 40mM. The sensitivity values of the In_2TiO_5 film above as-deposited and CF_4 plasma treatment at 60 sec samples were 1.55 and 2.69 mV/mM, respectively. Therefore, the In_2TiO_5 sensing membrane CF_4 plasma treatment at 60 sec has better sensitivity and linearity for urea detection.

Fig. 8 shows the glucose sensing properties of the In_2TiO_5 sensing membrane on EIS structure. From these figures, In_2TiO_5 film shows the sensitivity is 2.85 and 6.63 mV/mM in the concentration range between 2mM to 7mM. The In_2TiO_5 sensing membrane with CF_4 plasma treatment at 60 seconds has better sensitivity and linearity than as-deposited sample for glucose detection.

IV. Conclusion

In this study, the sensing membrane with CF_4 plasma treatment at 60 sec is improved biosensor device performance, such as excellent C-V curve, better hysteresis voltage, and smaller drift rate about 0.42 mV/hr. Therefore, the In_2TiO_5 sensing membrane with proper CF_4 plasma treatment is very promising for EIS biosensor applications.

V. References

[1]O. Bierwagen, J.S. Speck, Appl. Phys. Lett.106 (2010) 093704.
[2]D. Beena, K. J. Lethy, R. Vinodkumar, A.P. Detty, V.P. Mahadevanpillai, V. Ganesan, Optoelectron. Adv. Mat. 489 (2011) 215-223.

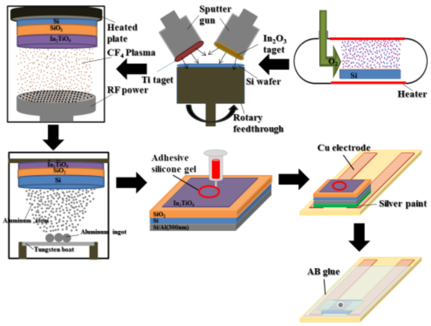

Fig. 1 The process flow of In_2TiO_5 sensing membrane with CF_4 plasma treatment.

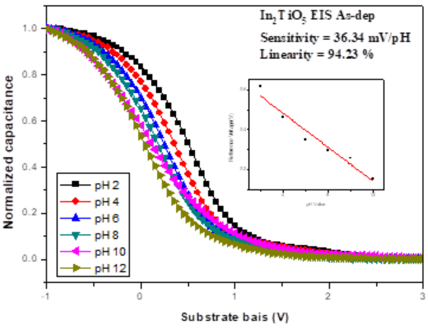

Fig. 2(a) In_2TiO_5 as-dep

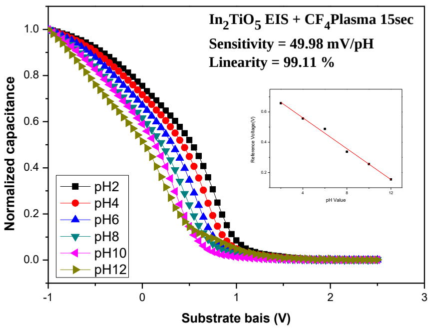

Fig. 2(b) In_2TiO_5 with CF_4 15sec

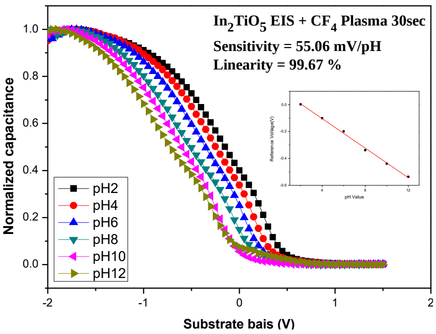

Fig. 2(c) In_2TiO_5 with CF_4 30sec

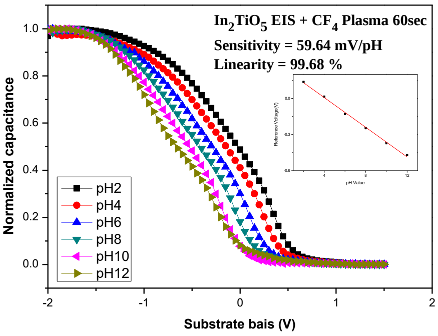

Fig. 2(d) In_2TiO_5 with CF_4 60sec

Fig. 2(a)-(d) The normalized C-V curve of the sample without and with CF_4 plasma treatment at various conditions, the inset figure represents the sensitivity and linearity.

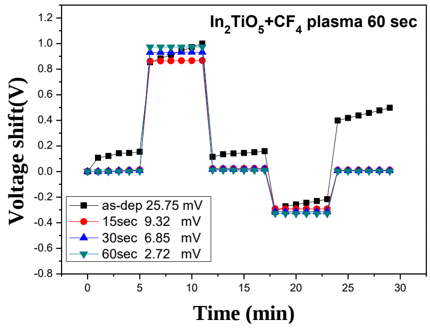

Fig. 3(a) The hysteresis of In_2TiO_5 sensing membrane with CF_4 plasma treatment at various conditions during the pH loop of 7→4→7→10→7 over a period of 30 minutes.

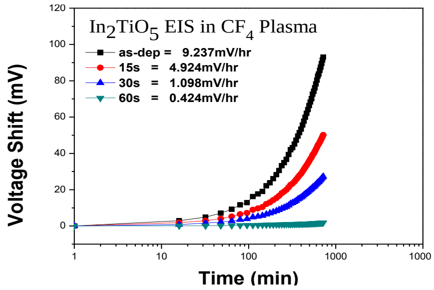

Fig. 3(b) The drift voltage of In_2TiO_5 sensing membrane annealed with CF_4 plasma treatment at various conditions, then dipped in pH 7 buffer solution for 12 hours.

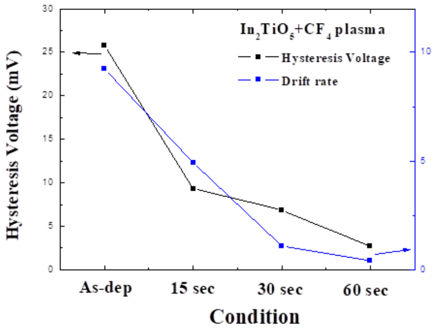

Fig. 3(c) Shows the samples with CF_4 plasma treatment at various conditions of hysteresis and drift rate.

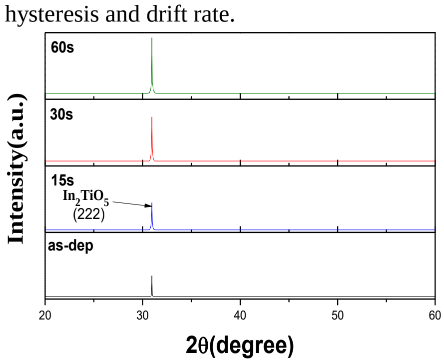

Fig. 4 XRD of the In_2TiO_5 film with CF_4 plasma treatment on single crystalline silicon

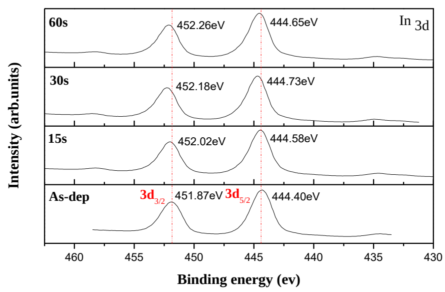

Fig. 5(a) XPS In 3d results of In_2TiO_5 film with CF_4 plasma treatment.

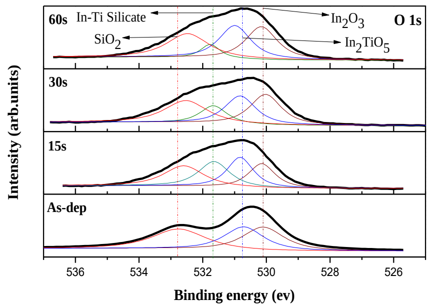

Fig. 5(b) XPS O 1s results of In_2TiO_5 film with CF_4 plasma treatment.

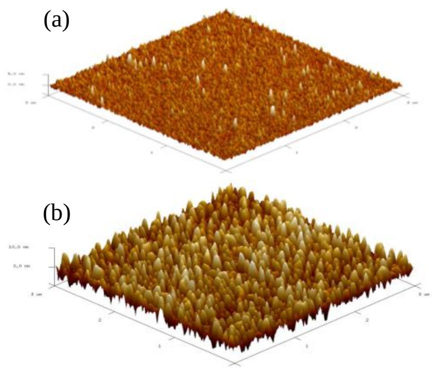

Fig. 6(a)-(b) (a) As-dep R_{rms}=0.62(nm), (b) CF_4 plasma at 60sec R_{rms}=2.92(nm)

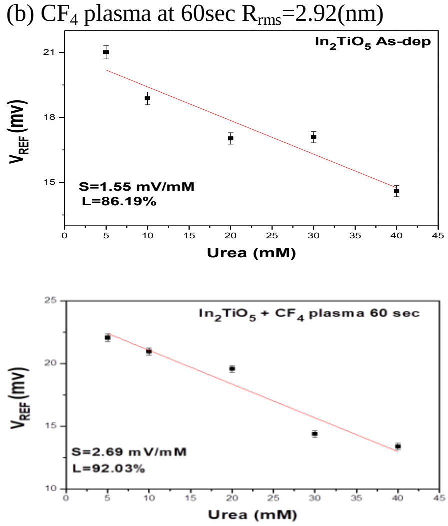

Fig. 7 pUrea-responses of enzyme-immobilized In_2TiO_5 as-dep and In_2TiO_5 with CF_4 plasma 60sec EIS structure by covalent bonding method.

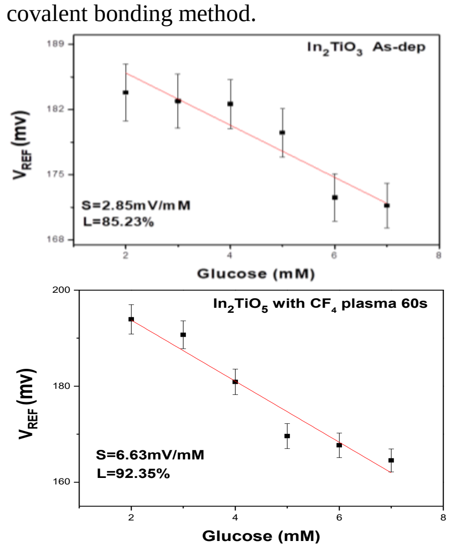

Fig. 8 pGlucose-responses of enzyme-immobilized In_2TiO_5 as-dep and In_2TiO_5 with CF_4 plasma 60sec EIS structure by covalent bonding method.