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The CeO_2 Sensing Membrane with NH_3 Plasma Treatment in Biosensor Applications

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Abstract- In the study, the electrolyte-insulator-semiconductor (EIS) biosensor device using CeO_2 sensing membrane and combined with NH_3 plasma treatment has been investigated. It can be found that the better sensing characteristics such as higher sensitivity (48.62 mV/pH) after plasma treatment at 3min, including lower hysteresis voltage, higher biosensor sensitivity , and higher linearity about 99.61%.

I. Introduction

Various high dielectric constant materials such as Gd_2O_3, Ta_2O_5, HfO_2 and Er_2O_3 [1] have been reported in EIS devices to substitute SiO_2 as a sensing membrane because of low cost, compatible with silicon, and small size. However, since high-k based devices are strongly dependent on fabrication processes, different treatments and alternative material compositions, intensive studies have investigated to achieve better ion sensing performance, smaller hysteresis, lower drift and higher stability to meet the requirement of commercial bio-medical industrial applications.

In this study, we discuss CeO_2 (k=20~26)[2-3] applied in EIS type combined with NH_3 plasma at different time. The physical analysis includes XRD (X-ray diffraction), XPS (X-ray photoelectron Spectroscopy) and AFM (Atomic Force Microscope). The electrical analysis includes the C-V curve, hysteresis voltage, drift rate and biosensor sensitivity.

II. Experiment

The EIS structures of a high-k CeO_2 sensing membrane were fabricated on 4-inch n-type (100) Si wafers. A 50 nm CeO_2 film was deposited on the Si substrate by means of sputtering from a gadolinium target in the ratio of Ar/O_2 = 25/0. Subsequently, samples were plasma treatment in NH_3 ambient for 1min, 3min and 6min. Then samples were annealed in N_2 ambient for 30 s by rapid thermal annealing (RTA) at various temperatures from 600℃. After that, the back-side contact of the Si wafer was deposited by Al film with 300nm-thick. Then, the sensing area was defined by standard photolithography process using a photosensitive epoxy, SU8-2005 of Micro Chem Inc. Finally, the samples were fabricated on the copper lines of printed circuit board (PCB) by 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 CeO_2 and sensing membrane by NH3 plasma treatment (1min to 6min) in buffer solution with various pH values. The sample of CeO_2 and treated in the plasma of 3min possessed the highest sensitivity. It showed that the capacitance value of the EIS device with NH_3 plasma treated at 6min is smaller than that of treated at 3min indicating the formation of a thicker amorphous Ce silicate layer at the CeO_2/Si interface. Therefore, the pH sensing membrane with a proper NH_3 plasma treatment at 3min can obtain an excellent linearity and high sensitivity. Fig.3(a)-(c) shows hysteresis voltage and drift rate under different NH_3 plasma treatment time conditions, and illustrates that the sample of CeO_2 film at 3min shows the lowest hysteresis voltage of 7.8 mV and the lowest drift rate of 0.51 mV/hr. Proper plasma treatment can repair bond connections, and repair the defects in the CeO_2 film by nitrogen incorporation.

Fig.4 shows the XRD spectra of high-k CeO_2 film before and after NH_3 plasma treatment samples. It can be seen that the NH_3 plasma treatment can induce crystallization in high-k sensing membrane, and the sample with NH_3 plasma treatment at 3min exhibited a stronger peak intensity in CeO_2 (400). Besides, in order to investigate the composition and chemical behaviors of high-k CeO_2 film, fig.5(a)-(b) shows the O 1s and Ce 3d XPS spectra of CeO_2 sensing membrane. In addition, the CeO_2 plasma treatment at 3min film can be seen the Ce 3d peak located at 881.6eV. Then O 1s spectra of CeO_2 film exhibited a smaller Ce-silicate peak intensity when the sensing membrane plasma treatment at 3min. This result indicates that the CeO_2 with NH_3 plasma at 3min could reduce SiO_2 and silicate formation.

Fig.6(a)-(b) shows AFM images of the CeO_2 sensing membrane for the as-deposited and NH_3 plasma treatment at 3min samples. The root mean square (rms) values of the above samples were 0.42 nm, and 0.56 nm, respectively. Because of interior grain size and structure, which became stronger and larger as NH_3 plasma treatment time increased.

Fig.7 shows the urea concentration controlled in a range between 5mM, and 40mM. The sensitivity values of the CeO_2 film above as-deposited and NH_3 plasma treatment at 3min samples were 2.42 and 3.81 mV/mM, respectively, Therefore, the CeO_2 sensing membrane NH_3 plasma treatment at 3min has better sensitivity and linearity for urea detection.

Fig.8 shows the glucose sensing properties of the CeO_2 sensing membrane on EIS structure. From these figures, CeO_2 film shows the sensitivity is 3.50 and 4.42 mV/mM in the concentration range between 2mM to 7mM. The CeO_2 sensing membrane with NH_3 plasma treatment at 3min has better sensitivity and linearity than as-deposited sample for glucose detection.

IV. Conclusions

In this study, the sensing membrane with NH_3 plasma treatment at 3min and annealed at 600°C can improve biosensor device performance, including excellent C-V curve, better hysteresis voltage, and smaller drift rate about 0.51 mV/hr. Therefore, the high-k CeO_2 sensing membrane with proper NH_3 plasma treatment is very promising for EIS biosensor applications.

V. References

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[2] Chun-Heng Chen, Ingram Yin-Ku, Joseph Ya-Min Lee, and Fu-Chien Chiu, *Appl. Phys. Lett. 92(2008), 043507.*

[3] Yi Wang, Feng Wei, Shoujing Yue, Zhimin Yang, and Jun Du, *Appl. Phys. Lett. 92(2008), 012915.*

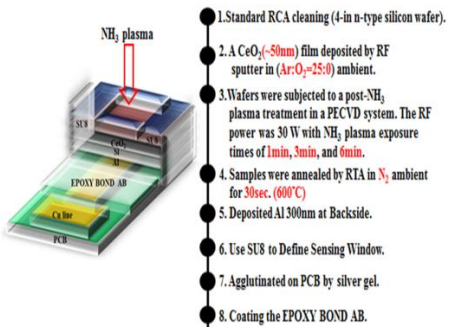

Fig. 1 The process flow of CeO_2 sensing membrane with NH_3 plasma treatment.

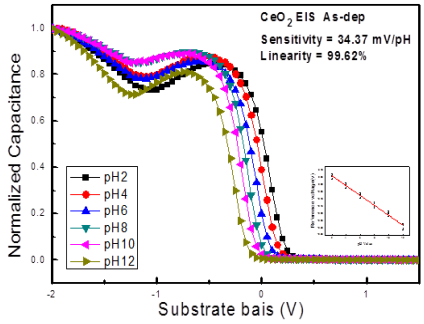

Fig. 2(a) CeO2 as-dep

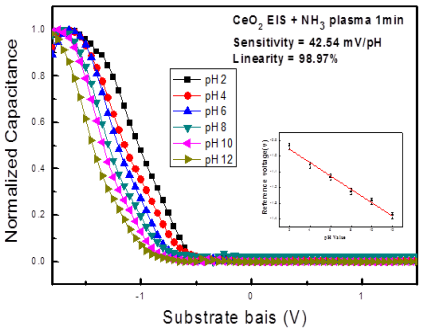

Fig. 2(b) CeO_2 with NH_3 1min

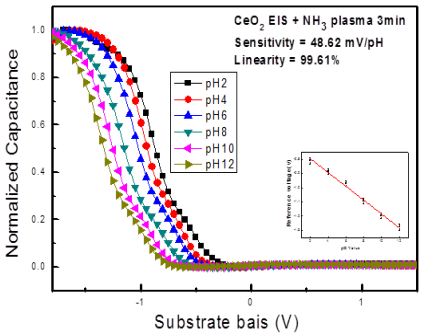

Fig. 2(c) CeO_2 with NH_3 3min

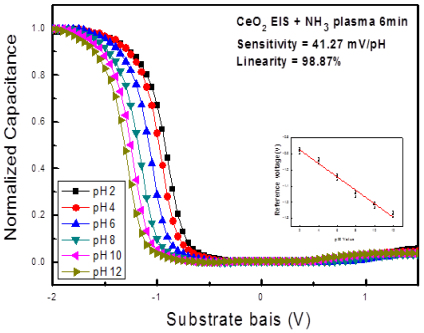

Fig. 2(d) CeO_2 with NH_3 6min

Fig. 2(a)-(d) The normalized C-V curve of the sample without and with NH_3 plasma treatment at various conditions, the inset figure represents the sensitivity and linearity.

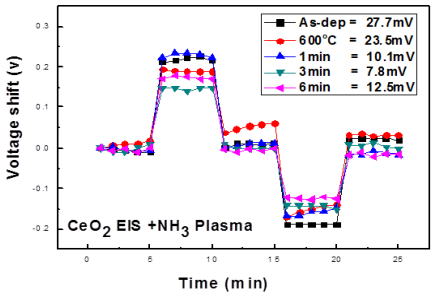

Fig. 3(a) The hysteresis of CeO_2 sensing membrane with NH_3 plasma treatment at various conditions during the pH loop of 7→4→7→10→7 over a period of 25 minutes.

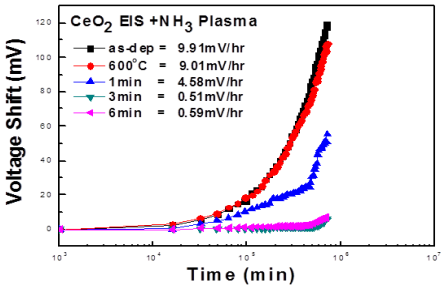

Fig. 3(b) The drift voltage of CeO_2 sensing membrane annealed with NH_3 plasma treatment at various conditions, then dipped in pH 7 buffer solution for 12 hours.

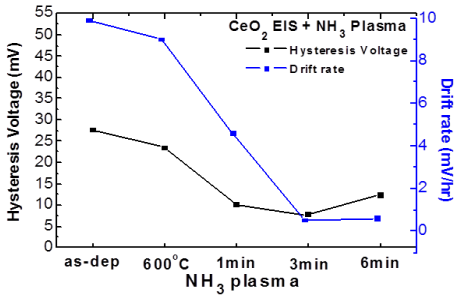

Fig. 3(c) Shows the samples with NH_3 plasma treatment at various conditions of hysteresis and drift rate.

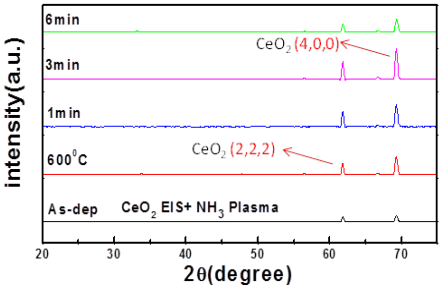

Fig. 4 XRD of the CeO_2 film with NH_3 plasma treatment on single crystalline silicon

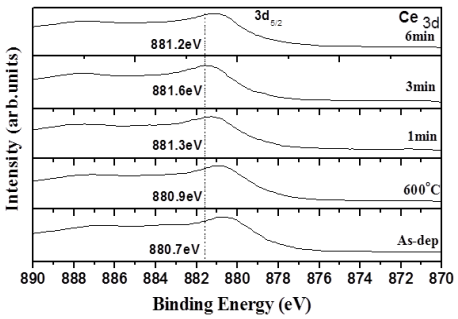

Fig. 5(a) XPS Ce 3d results of CeO_2 film with NH_3 plasma treatment.

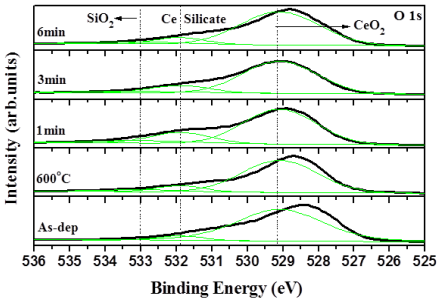

Fig. 5(b) XPS O 1s results of CeO_2 film with NH_3 plasma treatment.

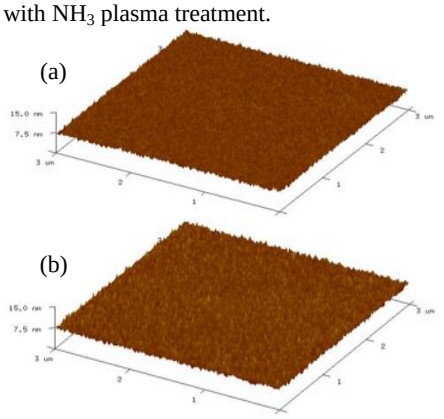

Fig. 6(a)-(b) (a) As-dep R_{rms}=0.42(nm), (b) NH_3 plasma at 3min R_{rms}=0.56(nm)

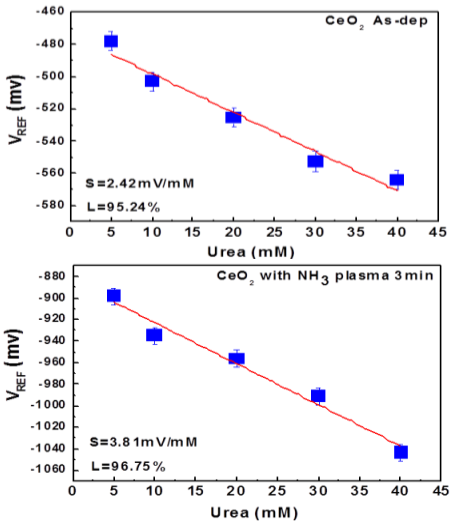

Fig. 7 pUrea-responses of enzyme-immobilized CeO_2 as-dep and CeO_2 with NH_3 plasma 3min EIS structure by covalent bonding method.

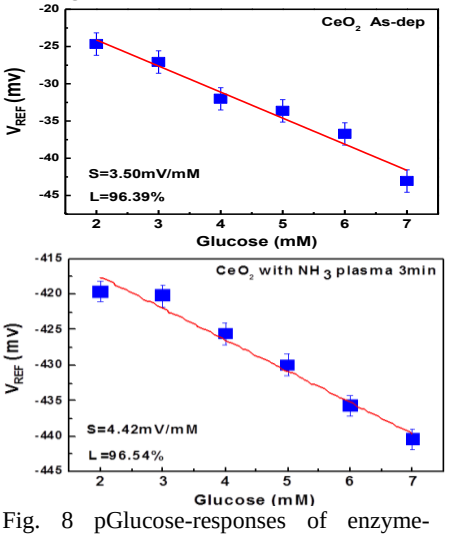

Fig. 8 pGlucose-responses of enzyme-immobilized CeO_2 as-dep and CeO_2 with NH_3 plasma 3min EIS structure by covalent bonding method.