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The Annealing Effect of $BaSrTiO_3$ Membrane in O_2 and N_2 Ambient for Electrolyte-Insulator-Semiconductor

Shan Wei Chang, Chyuan Haur Kao, Chun Fu Lin, Che Wei Chang, Chia Lun Chang, Yen Lin Su, Yu Xuan Huang
Department of Electronic Engineering, Chang Gung University,
259 Wen-Hwa 1st Road, Kwei-Shan Tao-Yuan 333, Taiwan, R.O.C.
Phone: +886-3-2118800 ext. 3314 E-mail: leo30055su@yahoo.com.tw

Abstract- In the paper, the EIS structure with high-k $BaSrTiO_3$ sensing film has more responsive to H^+ relative to Na^+ and K^+. The CeO_2 sensing membrane annealed with O_2 at 600^{o}C shows a higher sensitivity of 51.38 mV/pH, higher linearity, lower hysteresis voltage of 5.81 mV and lower drift rate of 2.21 mV/hr than the other conditions.

I. Introduction

Recently, the ISFET are very promising devices in vivo detect of ion activity in biomedical processes is due to the specific advantages, such as small size, low impedance, solid-state structure, and multiple ion-sensing capability [1]. In this study, we used the high-k $BaSrTiO_3$ as sensing membrane on EIS structure and to investigate the characteristics of the post RTA treatment in varied ambient (N_2, O_2). Furthermore, we studied the sensing performance of the $BaSrTiO_3$ EIS structure tested in different (Na^+, K^+, Urea, Glucose) solution .

II. Experiment

The EIS structures of a high-k $BaSrTiO_3$ sensing membrane were fabricated on 4-in n-type (100) Si wafers. A 50 nm $BaSrTiO_3$ film was deposited on the Si substrate by radio frequency reactive sputtering from a gadolinium target in the ratio of Ar/O_2 = 25/0. Subsequently, samples were annealed in O_2 ambient for 30 s by RTA at various temperatures from 600, 700, 800, 900 ℃. In addition, the others were annealed in N_2 ambient, which have the same RTA temperature in oxygen ambient. 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. Finally, the samples were fabricated on the copper lines of PCB by silver gel. Epoxy package was used to separate the EIS structure.

III. Results and Discussion

To research the crystalline structural and chemical formation of $BaSrTiO_3$ film annealing in O_2 and N_2 ambient effects, Fig.1(a-d) illustrate the Ba 3d, Sr 3d, O1s and Ti 2p spectra for the 600℃ and 700℃ sensing films in O_2 and N_2 ambient. Besides, Fig. 2(a-e) show AFM images of the $BaSrTiO_3$ films for post-RTA treatment at varied temperature for $BSTO_3$ films. The $BaSrTiO_3$ film annealed at 600℃ in O_2 ambient has higher surface roughness. The root mean square (rms) values for the samples in O_2 ambient and via RTA annealing from 600℃ to 700℃ are 2.254nm and 1.733nm, respectively. The film surface becomes smoother after the RTA temperature increased. We can see the difference in Fig. 2(e).

Besides, Fig. 3(a-d) show C-V curves in different conditions of RTA temperature (600℃ - 700℃) anneal in N_2 and O_2. The reference capacitance shift of the $BaSrTiO_3$ membrane annealed at 600℃ were 51.38mV/pH and 99.73% in N_2 ambient. Moreover, the threshold voltage shift of the $BaSrTiO_3$ membrane annealed at 600℃ were 54.70mV/pH in O_2 ambient. The hysteresis voltage of the above samples were show in Fig. 4. The hysteresis voltage of the RTA treatment for samples at 600℃ and 700℃ are 5.81 and 14.80mV in O_2 ambient which is better than 7.96 and 16.60mV in N_2 ambient. The drift effect of the $BaSrTiO_3$ sensing membrane was measured by C-V curve in pH 7 buffer solution for 12 hours as shown in Fig. 5. The drift rate of the sample annealed at 600 ℃ and 700 ℃ were 0.67 and 1.31mV/hr, respectively. It can be seen that the $BSTO_3$ sensing membrane after post-RTA treatment at 600^{o}C in oxygen ambient has lower drift rate than other samples. The comparison of $BaSrTiO_3$ sensing film applied in EIS structure after post-RTA treatment in different gas (N_2 or O_2) ambient for sensitivity, linearity, hysteresis voltage, and drift rate were shown in TABLE 1.

In addition, we compare the different ion sensitivity of $BaSrTiO_3$ sensing membrane annealed in different gas (N_2, O_2) ambient which were shown in Fig. 6 and Fig. 7. It can be seen that the EIS structure incorporating a high-K $BaSrTiO_3$ sensing film has more responsive to H^+ relative to Na^+ and K^+. Furthermore, the $BaSrTiO_3$ sensing membrane in O_2 ambient has higher H^+ selectivity than the other process. The covalent bonding steps were shown in Fig. 8. At first, the samples were put into 40^{o}C, 9% APTS solution for 4 hours for silylation. Then the samples were immersed into 10% of glutaraldehyde for 1 hour, which is a dual function group to crosslink amine bond on urease and ATPS. Final, enzyme was dripped on a sensing membrane and storage at 4^{o}C fridge overnight.

To study the urea and glucose sensing property of the $BaSrTiO_3$ sensing membrane on EIS structure, we prepared the solutions of urea and glucose which concentration were controlled in a range from 5mM~40mM and 2mM~7mM. Then, we picked the conditions of $BaSrTiO_3$ sensing membrane for RTA temperature at 600^{o}C in O_2 and N_2 ambient, the glucose and urea property as shown in Fig. 9(a-d). From that figures, show the sensitivity of RTA temperature at 600^{o}C in O_2 and N_2 ambient. The 600^{o}C samples in urea solution were 4.62mV/mM and 2.89mV/mM, the linearity were 95.57% and 95.22%. Besides, the 600℃ samples in glucose solution were 7.81 and 6.23mV/mM, the linearity were 96.26% and 95.76%. In this result, the $BaSrTiO_3$ sensing membrane with RTA temperature at 600℃ in O_2 ambient for urea detection has higher sensing properties.

IV. Conclusions

In this study, the $BaSrTiO_3$ sensing membrane after annealing at 600^{o}C in O_2 ambient shows a higher sensitivity, higher linearity, higher H^+ selectivity, lower hysteresis voltage and lower drift rate than the sample in N_2 ambient. Therefore, it can be confirmed, the $BaSrTiO_3$ sensing membrane with RTA treatment in O_2 ambient not only improved the bonding intensity and stabilized crystalline structure but also formed a stronger lattice to enhance the peak intensity.

V. References

[1] P. Bergveld, Development of an ion sensitive solid-state device for neurophysiological measurements, IEEE Trans. Biomed. Eng., vol.17 (1970)

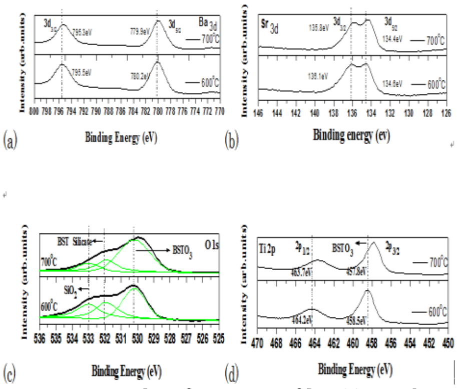

Fig. 1 XPS results of $BaSrTiO_3$ film (a)Ba 3d, (b)Sr 3d, (c)O 1s,(d)Ti 2p in O_2 ambient

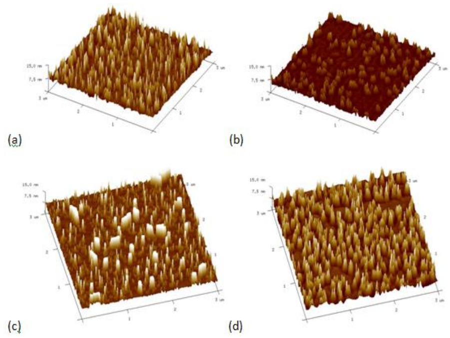

Fig. 2 AFM of high-k $BaSrTiO_3$ surface on single crystalline silicon after RTA at different temperatures (a) RTA 600°C in N_2 R_{rms}=1.312(nm) (b) RTA 700°C in N_2 R_{rms}=0.898(nm). (c) RTA 600°C in O_2 R_{rms}=2.254(nm) (d) RTA 700°C in O_2 R_{rms}=1.733(nm)

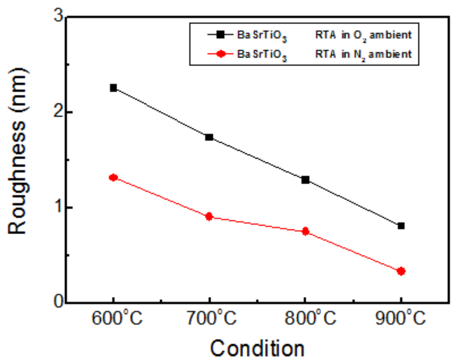

Fig. 2 (e) The comparison of AFM analysis for $BaSrTiO_3$ in different gas (N_2 or O_2)

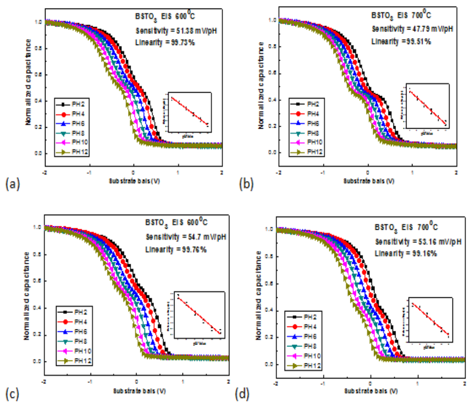

Fig. 3 The normalized C-V curve of the $BaSrTiO_3$ sensing membrane and with RTA (a)600°C (b)700°C annealing in N_2, and (c)600°C (d)700°C annealing in O_2 the inset figure represents the sensitivity and linearity.

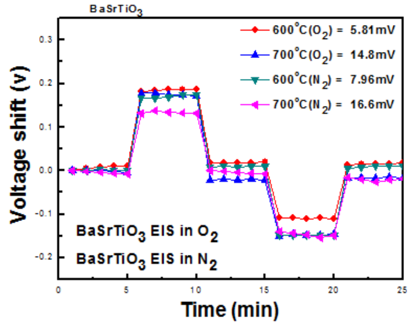

Fig. 4 Hysteresis of $BaSrTiO_3$ sensing membrane with various RTA temperatures in N_2 and O_2 ambient during the pH loop of 7→4→7→10→7 over a period of 25 minutes

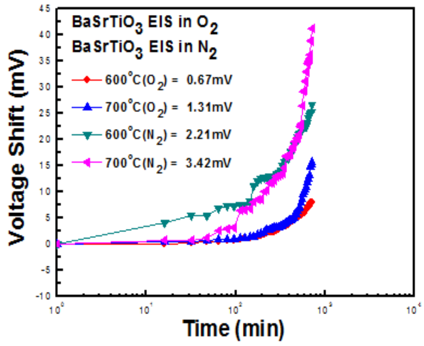

Fig. 5 Drift voltage of $BaSrTiO_3$ sensing membrane annealed with various RTA temperatures in N_2 and O_2 ambient, then dipped in pH 7 buffer solution for 12 hours

$BSTO_3$	600°C (O_2)	700°C (O_2)	600°C (N_2)	700°C (N_2)
Hysteresis voltage (mV)	5.81	14.80	7.96	16.60
Drift rate (mV/hr)	0.67	1.31	2.21	3.42

TABLE 1 The sensing performance of $BaSrTiO_3$ sensing membrane annealed at various RTA temperatures in N_2 and O_2 ambient

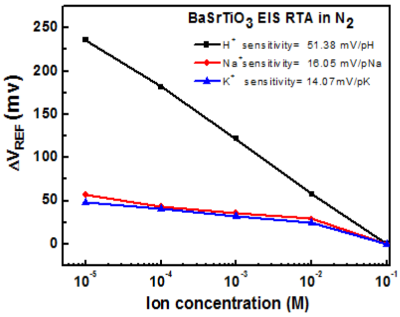

Fig. 6 The different ion sensitivity of $BaSrTiO_3$ sensing membrane annealed at 600°C in N_2 ambient

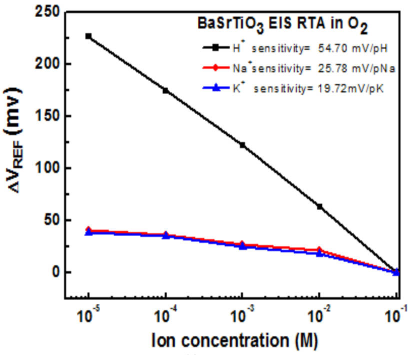

Fig.7 The different ion sensitivity of $BaSrTiO_3$ sensing membrane annealed at 600°C in O_2 ambient

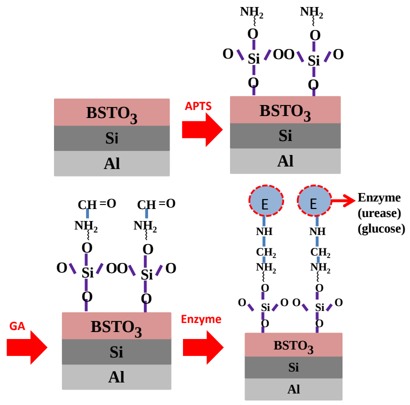

Fig. 8 Enzyme immobilization steps

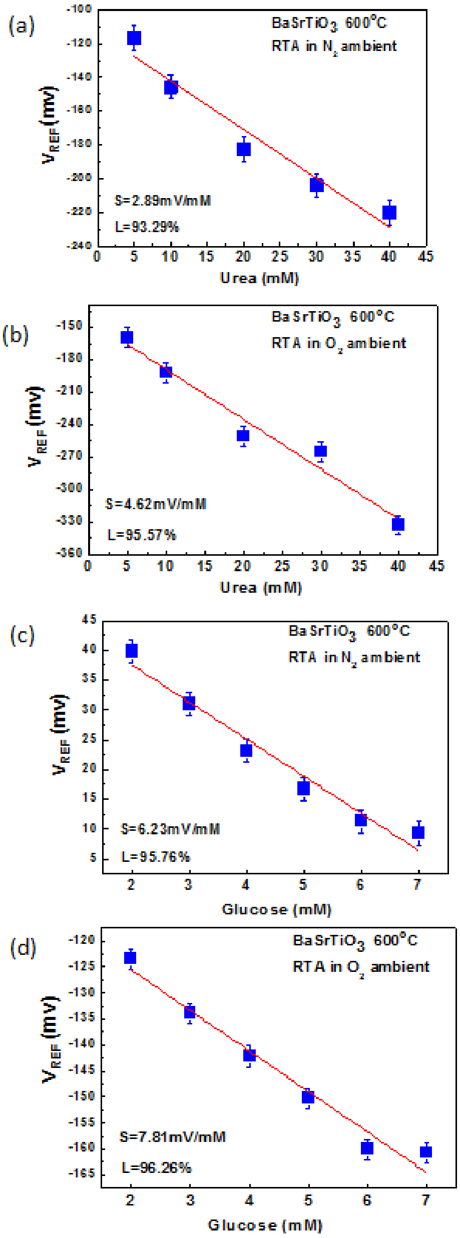

Fig. 9 The urea and glucose properties of RTA temperature at 600°C in O_2 and N_2 ambient.