The Annealing Effect of BaSrTiO₃ Membrane in O₂ and N₂ 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 BaSrTiO₃ sensing film has more responsive to H⁺ relative to Na⁺ and K⁺. The CeO₂ sensing membrane annealed with O₂ at 600°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 BaSrTiO₃ as sensing membrane on EIS structure and to investigate the characteristics of the post RTA treatment in varied ambient (N₂, O₂). Furthermore, we studied the sensing performance of the BaSrTiO₃ EIS structure tested in different (Na⁺, K⁺, Urea, Glucose) solution.

II. Experiment

The EIS structures of a high-k BaSrTiO₃ sensing membrane were fabricated on 4-in n-type (100) Si wafers. A 50 nm BaSrTiO₃ film was deposited on the Si substrate by radio frequency reactive sputtering from a gadolinium target in the ratio of Ar/O₂ = 25/0. Subsequently, samples were annealed in O₂ ambient for 30 s by RTA at various temperatures from 600, 700, 800, 900 °C. In addition, the others were annealed in N₂ 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 array 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 BaSrTiO₃ film annealing in O₂ and N₂ ambient effects, Fig.1(a-d) illustrate the Ba 3d, Sr 3d, O1s and Ti 2p spectra for the 600°C and 700°C sensing films in O₂ and N₂ ambient. Besides, Fig. 2(a-e) show AFM images of the BaSrTiO₃ films for post-RTA treatment at varied temperature for BSTO films. The BaSrTiO₃ film annealed at 600°C in O₂ ambient has higher surface roughness. The root mean square (rms) values for the samples in O₂ ambient and via RTA annealing from 600°C to 700°C are 2.54nm and 1.73nm, 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°C - 700°C) anneal in N₂ and O₂. The reference capacitance shift of the BaSrTiO₃ membrane annealed at 600°C were 51.38mV/pH and 99.73% in N₂ ambient. Moreover, the threshold voltage shift of the BaSrTiO₃ membrane annealed at 600°C were 54.70mV/pH in O₂ ambient. The hysteresis voltage of the above samples were show in Fig. 4. The hysteresis voltage of the RTA treatment for samples at 600°C and 700°C are 5.81 and 14.80mV in O₂ ambient which is better than 7.96 and 16.60mV in N₂ ambient.

The drift effect of the BaSrTiO₃ 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 °C and 700 °C were 0.67 and 1.31mV/hr, respectively. It can be seen that the BSTO sensing membrane after post-RTA treatment at 600°C in oxygen ambient has lower drift rate than other samples. The comparison of BaSrTiO₃ sensing film applied in EIS structure after post-RTA treatment in different gas (N₂ or O₂) ambient for sensitivity, linearity, hysteresis voltage, and drift rate were shown in Table 1.

In addition, we compare the different ion sensitivity of BaSrTiO₃ sensing membrane annealed in different gas (N₂, O₂) ambient which were shown in Fig. 6 and Fig. 7. It can be seen that the EIS structure incorporating a high-K BaSrTiO₃ sensing film has more responsive to H⁺ relative to Na⁺ and K⁺. Furthermore, the BaSrTiO₃ sensing membrane in O₂ 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°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 APTS. Finally, enzyme was dripped on a sensing membrane and storage at 4°C fridge overnight.

To study the urea and glucose sensing property of the BaSrTiO₃ 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 BaSrTiO₃ sensing membrane for RTA temperature at 600°C in O₂ and N₂ ambient, the glucose and urea property as shown in Fig. 9(a-d). From that figures, show the sensitivity of RTA temperature at 600°C in O₂ and N₂ ambient. The 600°C samples in urea solution were 4.62mV/mM and 2.89mV/mM, the linearity were 95.57% and 95.22%. Besides, the 600°C samples in glucose solution were 7.81 and 6.23mV/mM, the linearity were 96.26% and 95.76%. In this result, the BaSrTiO₃ sensing membrane with RTA temperature at 600°C in O₂ ambient for urea detection has higher sensing properties.

IV. Conclusions

In this study, the BaSrTiO₃ sensing membrane after annealing at 600°C in O₂ ambient shows a higher sensitivity, higher linearity, higher H⁺ selectivity, lower hysteresis voltage and lower drift rate than the sample in N₂ ambient. Therefore, it can be confirmed, the BaSrTiO₃ sensing membrane with RTA treatment in O₂ ambient not only improved the bonding intensity and stabilized crystalline structure but also formed a stronger lattice to enhance the peak intensity.

V. References

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$_2$, $R_{	ext{rms}}=0.898$ nm. (b) RTA 700°C in N$_2$, $R_{	ext{rms}}=2.254$ nm. (c) RTA 600°C in O$_2$, $R_{	ext{rms}}=1.733$ nm.

Fig. 2 (c) 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.

<table>
<thead>
<tr>
<th>RTA Temperature (°C)</th>
<th>N$_2$</th>
<th>O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>5.81</td>
<td>14.80</td>
</tr>
<tr>
<td>700</td>
<td>7.96</td>
<td>16.60</td>
</tr>
</tbody>
</table>

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.