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Electrolyte-Insulator-Semiconductor (EIS) with Gd_2O_3-based Sensing Membrane for pH-Sensing Applications

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Abstract: Gd_2O_3 as pH sensing membrane on Si substrate treated with annealing for the electrolyte-insulator-semiconductor has been fabricated. The high-k sensing membrane can obtain high sensitivity, high linearity, low hysteresis voltage, and low drift rate. The high-k Gd_2O_3 pH sensing membrane show promise for future industrial sensing device applications.

Keywords: Gd_2O_3, annealing, electrolyte-insulator-semiconductor, sensing membrane, pH value

1. INTRODUCTION

Since the first ion-sensitive field-effect transistor (ISFET) was invented, a sensor used to measure numerous chemical compounds in solution was developed to measure pH and ion concentrations [1]. The advantages of ISFETs are numerous, including relatively small in size, rapid response, high-impedance output and lower production cost. A standard ISFET consists of an electrolyte and SiO_2, with the electrolyte solution in direct contact with the gate insulator layer and a reference electrode in the solution replacing a metal gate to form an electrolyte-insulator-semiconductor (EIS) structure. The design of an ISFET is an integration of electrolyte and SiO2, as the sensing membrane, which replaces the traditional metal gate, to build an EIS structure. Given that gadolinium oxide (Gd_2O_3) has high chemical and thermal stability, Gd_2O_3 has a dielectric constant k of around 15, a wide band gap and a large conduction band offset, a protective and corrosion-resistant coating as a gate dielectric [2]; as pH sensing membrane on silicon, Gd_2O_3 can undergo a high-temperature rapid thermal annealing (RTA) for the EIS applications. Based on previous studies [3, 4] annealing can reduce the dangling bonds and fill the traps between the interface. Some ions may attach to the dangling bonds and traps because of the electrical attraction force. Decreasing the dangling bonds and traps and hence improve the crystalline structure can cause the sensitivity and linearity better because so the factor of the interfering ions can be removed. The high-k Gd_2O_3 sensing membrane with RTA has advantages of high sensitivity, high linearity, low hysteresis voltage, and low drift rate due to improvements of crystalline structures [5, 6].

2. EXPERIMENTAL METHODS

The electrolyte-insulator-semiconductor (EIS) devices were constructed using Gd2O3 5 sensing membranes on a 4-in p-type (1 0 0) Si wafers, the resistivity of which is 5 to 10Ω-cm (Well-Being Enterprise Co.). Native oxide on the surface of samples were remove by dipping into 1% hydrofluoric acid after a standard RCA clean process . A ~25nm Gd_2O^3 film was deposited on Si substrate through reactive sputtering from a Gadolinium target in diluted O_2. Samples were annealed at different temperatures (700℃.800℃, and 900℃) by rapid thermal annealing (RTA) in O_2 ambient for 30 sec. The back-side contact of the Si wafer was deposited by Al film with 300nm-thick. Then sensing membrane size was defined through photolithographic processing under a photosensitive epoxy (SU8-2005, Micro Chem Inc.) functioning as an antacid polymer. EIS devices were then fabricated on the copper lines of a printed circuit board by using a silver gel to form conductive lines. The EIS structure and the copper line were en-

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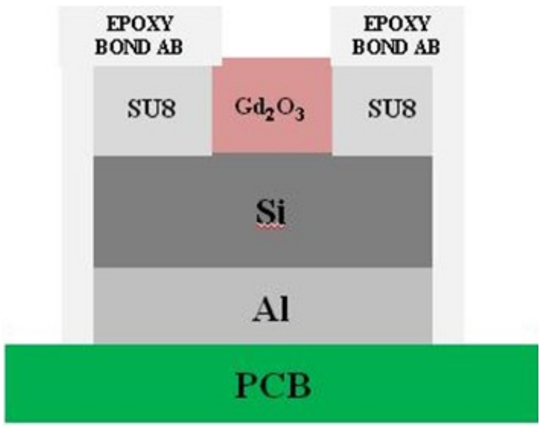

Figure 1. The process of Gd_2O_3 EIS structure.

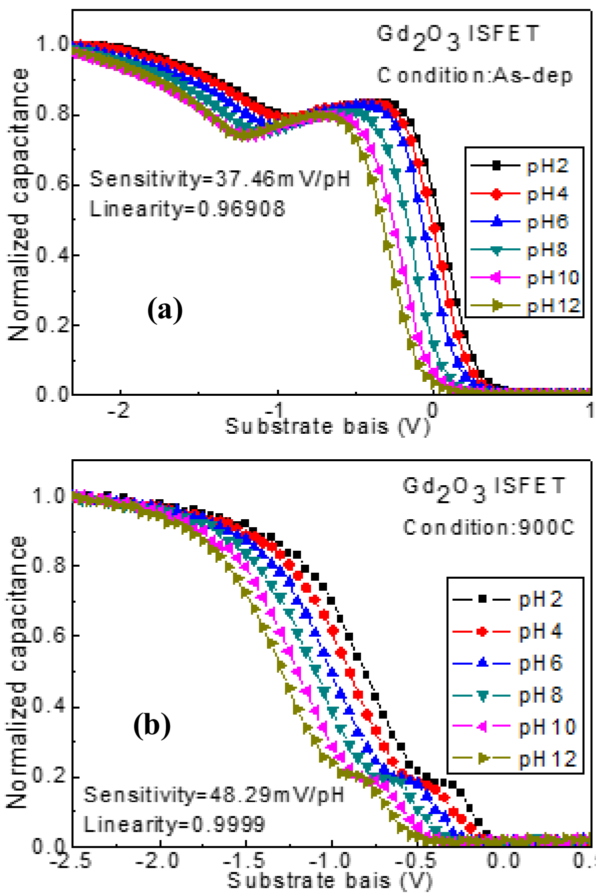

Figure 2. The normalized C-V curve of the sample.

capsulated by a costum-made epoxy package . The physical properties of the high-k Gd2O3 sensing membrane are analyzed by Atomic Force Microscopy (AFM). Besides, the most preferable condition for the sensor performance was evaluated, via PH sensitivity, hysteresis, and drift rate by HP 4284 meter.

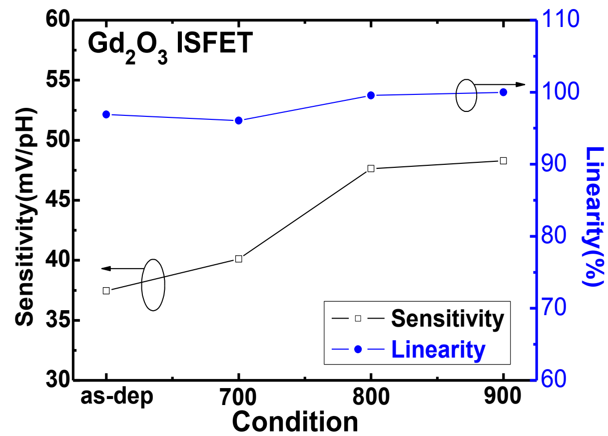

Figure 3. Comparison of different RTA conditions of sensitivity and linearity.

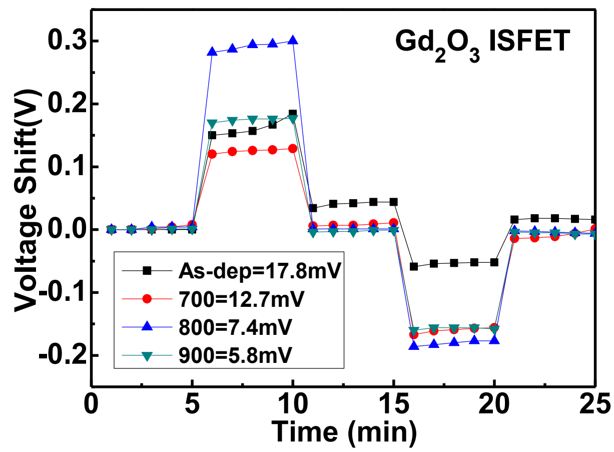

Figure 4. Hysteresis of Gd_2O_3 sensing membrane with various PDA temperatures treatment during the pH loop of 7→4→7→10→7 over a period of 50 minutes.

3. RESULTS AND DISCUSSION

The device structure of the Gd_2O_3, pH sensing membrane based electrolyte-insulator-semiconductor on printed circuit board (PCB) is shown in Fig.1. In pH-EIS sensing, the change in pH of the solution led to a shift in the flat belt voltage of the C-V curves. This result is primarily due to the ionization of the surface hydroxyl groups by either hydrogen ions or hydroxyl ions. To evaluate the sensing performance of the Gd_2O_3 EIS device annealed at difference temperatures, the C–V curves were taken from the as-deposited (control) and 900 °C annealed EIS devices immersed for 30 s in buffer solutions from pH 2 to pH 12 values as shown in Fig. 2(a) and (b). The comparison of different as-deposited RTA annealing from 600°C to 900°C which conditions of sensitivity and linearity of the samples are shown in Fig. 3(a). We can see the sensitivity and linearity of the Gd_2O_3 sensing membrane annealed at 900 ºC has the highest sensitivity and the second highest linearity. Anneal-

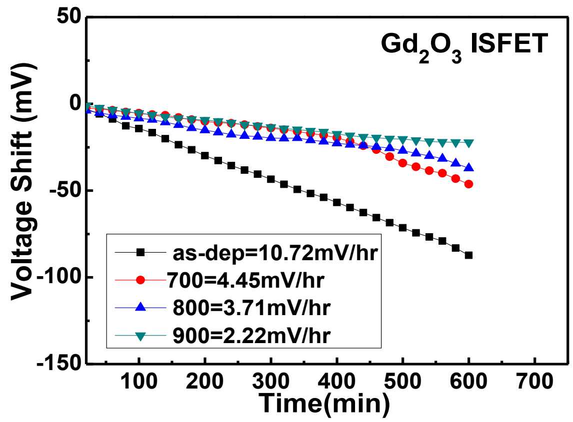

Figure 5. Drift voltage of Gd_2O_3 sensing membrane with various PDA temperatures treatment in pH 7 buffer solution for 10 hours.

ing at 900 ºC can improve the sensing performance of the membrane. Hysteresis phenomenon can be explained by the defects of an insulator film, causing the formation of porous structures. The interior sites of these porous detects could react with the ions existing in the tested solution and thus results in hysteresis response. Another possible cause is the interaction of ions in the tested solution with the responding sites along the boundaries of grains on an insulator film. Hysteresis of Gd_2O_3 EIS sensing membrane treated with various temperatures during the pH loop of 7→4→7→10→7 over a period of 25 minutes is shown in Fig. 4. The hysteresis voltages of the as-deposited and the RTA-annealed samples at 700,800, and 900 ºC were 12.7, 7.4, and 5.8 mV, respectively; the sample annealed at 900 ºC had the least deviation. The dangling bonds and the defects of the membrane attach the ions, which suppress the diffusion of reacting ions and delay reference voltage response. RTA annealing could remove the trap and passive the dangling bonds. Finally, for long-term use of the sensor device, the drift effect of Gd_2O_3-EIS sensing membrane was analyzed by discrete I-V measurement in buffer solution for 10 hours immersion. The drift rate of the as-deposited sample and the sample annealed at 700, 800 and 900 ºC were 4.45, 3.71, and 2.22 mV/hr, respectively [7, 8]. In long-term measurements, the sensing membrane might react with H_2O and have weakly bonded ion on the surface of sensing membrane. Therefore, the traps and the dangling bonds on the surface of the membrane may gradually capture clusters of ions on the surface which cause the reference voltage drift of the device. Annealing can improve the crystalline structures and hence cause the EIS with high sensitivity, high linearity, low hysteresis voltage, and low drift rate. The study shows Gd_2O_3 membrane annealed at 900 ºC with good electrical reliability could attain the most favorable pH, sensitivity, linearity, hysteresis voltage and drift rate.

4. CONCLUSION

This research concludes the Gd_2O_3 sensing membrane deposited on EIS structure with improved material quality with RTA treatment could achieve high sensitivity, higher linearity, low hysteresis voltage, and low drift ratio. The EIS device annealed at 800 °C or 900 °C could obtain the most preferable sensing capability among all the devices due to reinforcement of crystalline structures and few crystal defects for future sensor applications. In this condition, material analysis and sensor performance had the most preferable properties. The Gd_2O_3 sensing membrane shows promise for future commercial sensor applications.

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