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Analyzing the effect of Rapid Thermal Annealing on Mg-doped ZnO EIS Structure Membrane for Na^+ and K^+ Sensing

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Abstract- In this study, the pH and ion-concentration sensing properties of an electrolyte insulator semiconductor (EIS) device based on magnesium-doped ZnO are investigated. The highest sensitivity toward pH (59.29 mV/pH) and ion concentrations, smallest hysteresis (3.82 mV), and lowest drift rate were observed for the Mg-doped sample annealed at 700 °C. EIS devices based on Mg-doped ZnO could be used as excellent sensors for future biomedical applications.

I. Introduction

Zinc oxide is a wide-bandgap (Eg = 3.3 eV) n-type semiconductor with a tetragonal crystal structure10, widely used in gas sensors, solar cells, and lithium batteries. Particularly, it is used to detect hydrogen gas with high accuracy in a wide range of concentrations. As pH sensors work by detecting the amount of hydrogen ions in solution, ZnO has the potential for pH sensing owing to its excellent sensitivity to hydrogen. Moreover, in this study, an alternative doping method of co-sputtering was employed to include magnesium oxide (MgO) clusters into the sensing layer and optimize the sensing behavior. Magnesium oxide is a wide-bandgap material (~7.6 eV), and the low electronegativity of Mg (χ = 1.31)[1] increases the tendency to form stable crystalline structures with oxygen.

II. Experiment

The sensing devices were fabricated on n-type (100) silicon wafers, after cleaning by the regular RCA clean process. Mg-doped ZnO sensing membranes of thickness 50 nm each were deposited on the silicon wafer by radio frequency (RF) reactive sputtering and co-sputtering, respectively, in an atmosphere consisting of a mixture of Ar and O_2 (20:5). After the deposition, rapid thermal annealing (RTA) at temperatures of 600 °C to 800 °C in O_2 atmosphere was carried out for 30 s. After annealing, a 300 nm Al film was evaporated on the reverse of the silicon wafer. An adhesive silicone gel was used to define the sensing window on the membrane. Finally, the samples were attached on the copper strips of a printed circuit board with silver gel, and an epoxy package was used to insulate the EIS structure from the copper line. The detailed fabrication process is illustrated in Fig. 1.

III. Results and Discussion

To determine the optimal conditions for the EIS membrane treatment, pure and Mg-doped ZnO samples post RTA at 600 °C to 800 °C were compared. Based on the cyclic voltammetry (C-V) curves, their sensitivity and linearity were extracted. The C-V curves for the as-deposited Mg-doped ZnO and the Mg-doped ZnO device annealed at 700 °C are shown in Figs. 2 (a) and (b), respectively. According to all the C-V curves and extracted data, the Mg-doped device annealed at 700 °C has the highest sensitivity of 59.29 mV/pH and a high linearity of 99.80 %, indicating that Mg doping and appropriate annealing could enhance the sensing performance. Fig. 3(a)-(c) shows hysteresis voltage and drift rate under different annealing temperature conditions, and illustrates the lowest hysteresis voltage of 3.82 mV and the lowest drift rate showed 0.53 mV/hr for the sample annealed at 700 °C. However, due to the low electronegativity of Mg (χ = 1.31), Mg^{2+} ions are easily formed. When Mg^{2+} is doped into the ZnO film, the substitution of Mg^{2+} ions for Zn^{2+} ions can modify the Zn-O bonding and enhance the surface site density. As a result, the pH response increases drastically.

Fig. 4 (a)-(c) shows The O1s XPS profile can be deconvoluted into peaks centered at 533.0, 531.5, 529.6, and 530.2 eV corresponding to SiO_2, Mg-Zn silicate[2], ZnO, and Mg-doped ZnO, respectively. These results indicate that the sample annealed at 700 °C has the strongest Mg-doped ZnO signal compared to that of the other RTA conditions and intensity of the XPS-peaks increases with the temperature. It can also be observed that the sample treated at 700 °C has the lowest silicate signal compared to that of the all condition. This can be possible due to reduction of dangling bonds or defects formation during annealing. Annealed Mg-doped samples have lower silicate concentration, and the XPS signal indicates less dangling bonds and porous defects. Therefore, stability in terms of hysteresis voltage and drift voltage deviation could be achieved (Fig. 3).

Two-dimensional (2D) AFM images of the as-deposited and RTA-treated Mg-doped ZnO samples are shown in Figs. 5 (a)-(d). The Mg-doped ZnO film annealed at 700 °C has the highest root mean squared (rms) surface roughness of 4.26 nm. As Mg possesses a higher affinity toward O, the incorporation of Mg atoms enhances the formation of grains to improve the sensing performance.

To study the sensing efficiency of the devices for sodium and potassium ions, 1 M NaCl/Tris–HCl and 1 M KCl/Tris–HCl were added into buffer electrolyte with concentrations of sodium and potassium ions between 10^{-5} and 10^{-1} M. The sensitivity and linearity of the as-deposited ZnO sample, the ZnO sample annealed at 600 °C, the as-deposited Mg-doped sample, and the Mg-doped ZnO sample annealed at 700 °C towards sensing Na^+ and K^+ ions are shown in Fig. 6. The Mg-doped ZnO sample annealed at 700 °C has the highest sensitivity and linearity for both sodium and potassium ion sensing, in line with pH sensing results.

IV. Conclusion

In this study, the sensing membrane with rapid thermal annealing at 700℃ can improve biosensor device performance, including excellent C-V curve, better hysteresis voltage, and smaller drift rate about 0.53 mV/hr. Therefore, the Mg-doped ZnO sensing membrane with proper rapid thermal annealing is very promising for EIS biosensor applications.

V. References

[1] C.-H. Kwak, H.-S. Woo, F. Abdel-Hady, A.A. Wazzan, J.-H. Leea, Sens. Actuators B 223, 527-534 (2016).
[2] C. Lin, H. Zhang, J. Zhang and C. Chen, Sensors. 19, 519 (2019).

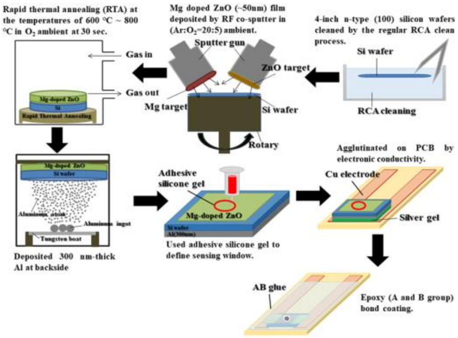


Fig. 1 Schematic of the fabrication process of Mg-doped ZnO sensing membrane.

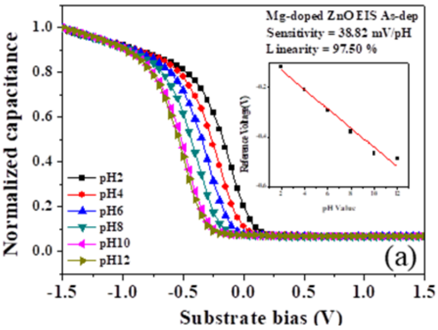


Fig. 2(a) Mg-doped ZnO as-dep

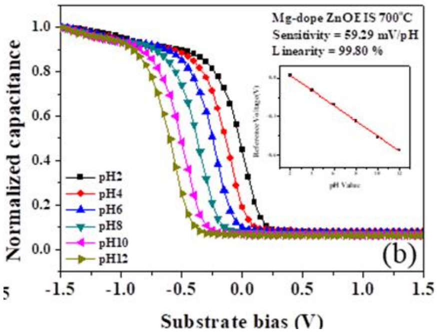
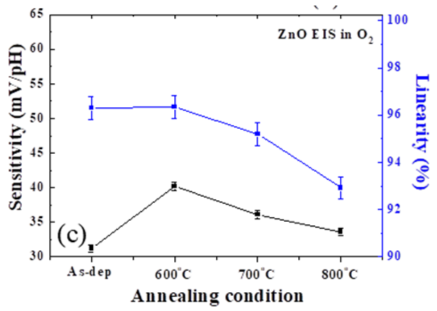


Fig. 2(b) Mg-doped ZnO 700℃



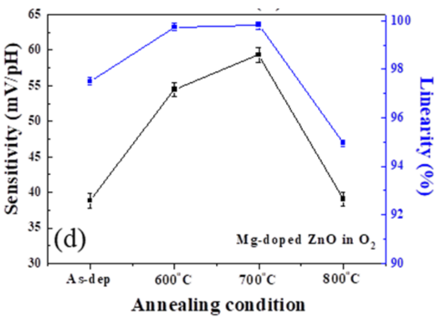


Fig. 2(a)-(d) Cyclic voltammetry curves of Mg-doped ZnO films (a) as-deposited and (b) annealed at 700 ℃ when immersed in solution with pH values from 2 to 12. Sensitivity and linearity of EIS devices with (c) pure ZnO and (d) Mg-doped ZnO as a function of RTA temperatures.

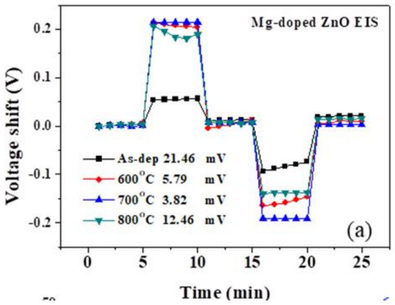


Fig. 3(a) Hysteresis of Mg-doped ZnO films during the pH loop of 7→4→7→10→7 over a period of 25 minutes.

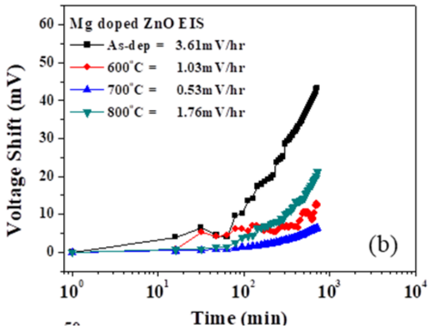


Fig. 3(b) Drift voltage of Mg-doped ZnO films dipped in pH 7 buffer solution for 12 hours.

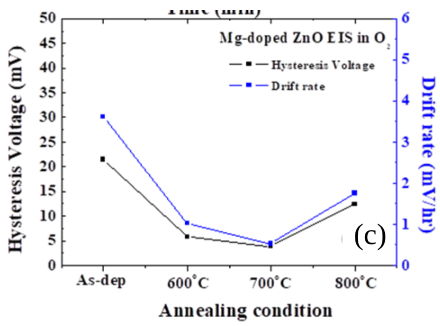
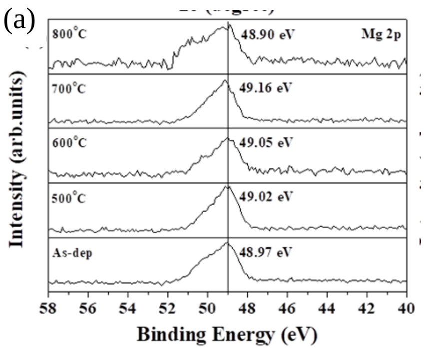


Fig. 3(c) Shows the samples with rapid thermal annealing at various conditions of hysteresis and drift rate.



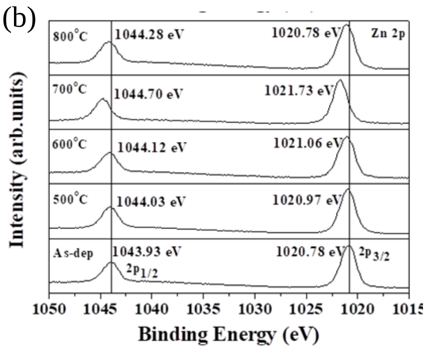


Fig. 4(a)-(b) XPS Zn 2p and Mg 2p results of Mg-doped ZnO film with rapid thermal annealing..

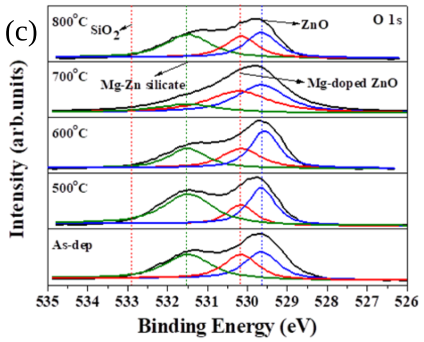


Fig. 4(c) XPS O 1s results of Mg-doped ZnO film with rapid thermal annealing.

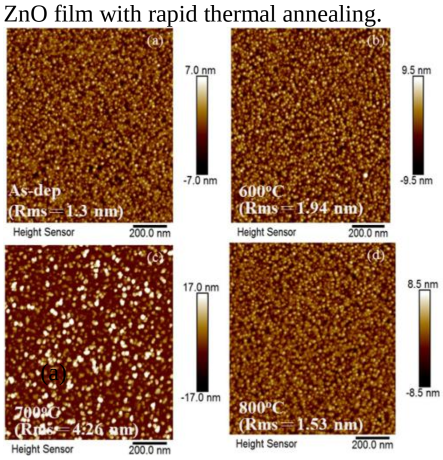


Fig. 5(a)-(b) (a) As-dep R_{rms}=1.3(nm), (b) RTA at700℃ R_{rms}=4.26(nm)

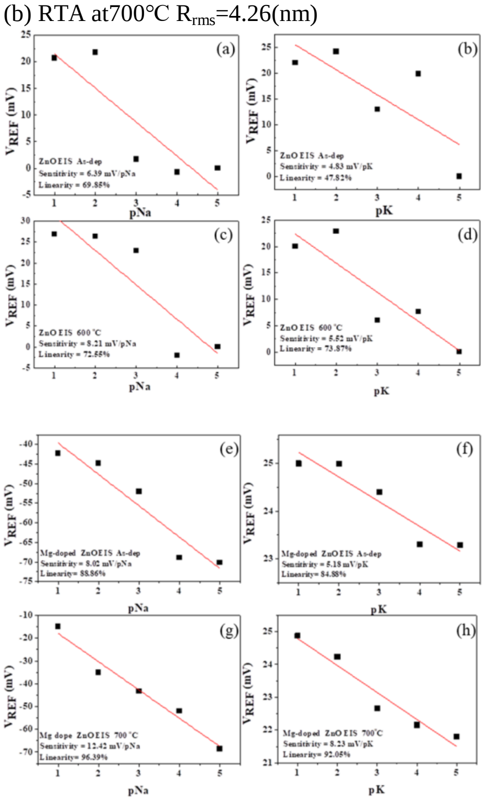


Fig. 6 Sensitivity and linearity of ZnO and Mg-doped ZnO sensing membranes toward sodium and potassium ions.