明新學報 44 卷 第 2 期 PP.129-134
Vol. 44, No. 2, Mghsin Journal, Dec. 2021

The ZrO_2 Sensing Membrane in Electrolyte-Insulator- Semiconductor for Bio-Sensor Applications

Ming Ling Lee[1], Hsin Yuan Wang[2], Chyuan Haur Kao[2], Phan Thi My Kien[1], Shih-Lun Hsieh[1]
[1]Department of Electro-Optical Engineering, Minghsin University of Science and Technology,
No.1, Xinxing Rd., Xinfeng Hsinchu 30401, Taiwan, R.O.C.
[2]Department of Electronic Engineering, Chang Gung University,
259 Wen-Hwa 1st Road, Kwei-Shan Tao-Yuan 333, Taiwan, R.O.C.
mingling@must.edu.tw

Abstract

Various kinds of high-k metal oxide materials such as, Gd_2O_3, Ta_2O_5, HfO_2, Er_2O_3, and Yb_2O_3 have been reported in electrolyte insulator semiconductor (EIS) devices because of their good sensing performance. However, this structure is not stable after long-term measurement because generate interface layer between high-k metal oxide and silicon during high-temperature process. Therefore, the high-k metal oxides with post rapid thermal annealing exhibited a thinner interfacial layer, higher capacitance value and lower leakage current for performance improvements.

In the paper, the high-k ZrO_2 was used as sensing membrane of electrolyte-insulator-semiconductor (EIS) structure for sensor applications. According to the result, this sensor device with RTA 900ºC annealing can get the best sensor characteristics such as sensitivity of 51.84 mV/pH and hysteresis voltage of 6.56 mV and 4.82 mV/hr drift rate among all conditions.

Key words：high-k, EIS, ZrO_2, sensing membrane

1. Introduction

Various kinds of high-k metal oxide materials such as, Gd_2O_3, Ta_2O_5, HfO_2, Er_2O_3, and Yb_2O_3 [1-9] have been reported in electrolyte insulator semiconductor (EIS) devices because of their good sensing performance. However, this structure is not stable after long-term measurement because generate interface layer between high-k metal oxide and silicon during high-temperature process. Therefore, the high-k metal oxides with post rapid thermal annealing exhibited a thinner interfacial layer, higher capacitance value and lower leakage current for performance improvements. [11-14]

In the paper, the high-k ZrO_2 was used as sensing membrane of EIS structure for pH sensor applications. It can be found that the sensor device with RTA 900ºC annealing can get the best sensor characteristics such as sensitivity of 51.84 mV/pH and hysteresis voltage of 6.56 mV and 4.82 mV/hr drift rate among all conditions.

2. Experiment

The EIS structures of a high-k ZrO_2 sensing membrane were fabricated on 4-in n-type (100) Si wafers. Before the deposition of ZrO_2 film, the wafers were cleaned using a standard RCA process and then they were treated with 1% HF to remove the native oxide. A 30 nm ZrO_2 film was deposited on the Si substrate by means of sputtering from a zirconium dioxide target in the ratio of Ar/O_2 =15/10. Subsequently, samples were annealed in O_2 ambient for 30 s by rapid thermal annealing (RTA) at various temperatures from 600, 700, 800, 900 ºC. The RTA was heated at a rate of 30ºC/sec before reaching the target temperature. The backside contact (a 300-nm-thick Al film) of the Si wafer was deposited using a thermal coater. The sensing membrane size was defined through photolithographic processing under a photosensitive epoxy (SU8-2005, MicroChem) that behaved as an anti-acid polymer. EIS devices were then fabricated on the Cu lines of a printed circuit board by using a Ag gel to form conductive lines. A handmade epoxy package was employed to encapsulate the EIS structure and the Cu line. The detail EIS structure was illustrated in Fig.2

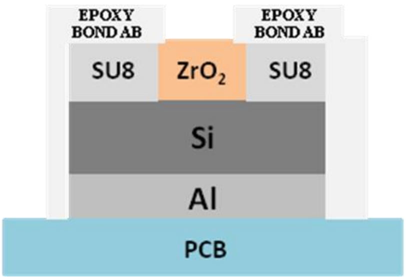


Fig.1 The ZrO_2 EIS structure

3. Results and Discussion

Fig. 2 show the XRD spectra of ZrO_2 samples under various annealing conditions in O_2 ambient. The peak intensity was increasing as the temperature raises and the sample with highest RTA temperature of 900ºC clearly exhibited a stronger peak of (120) was shown in the spectra. To research the crystalline structural and chemical formation of ZrO_2 film due to annealing in O_2 ambient effects, Fig. 3 (a) and (b) illustrate the Zr 3d, O 1s XPS spectra for the as-deposited and annealed films at various temperatures. [15-17]

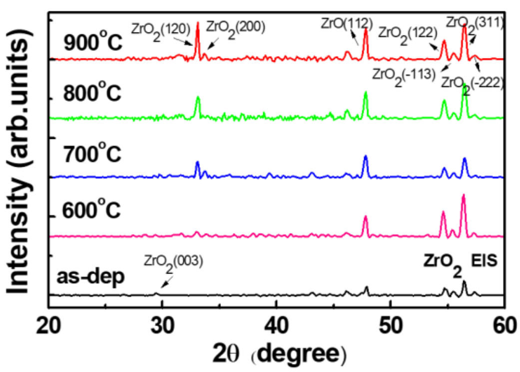


Fig.2 XRD of the ZrO_2 film after RTA annealing at various temperatures.

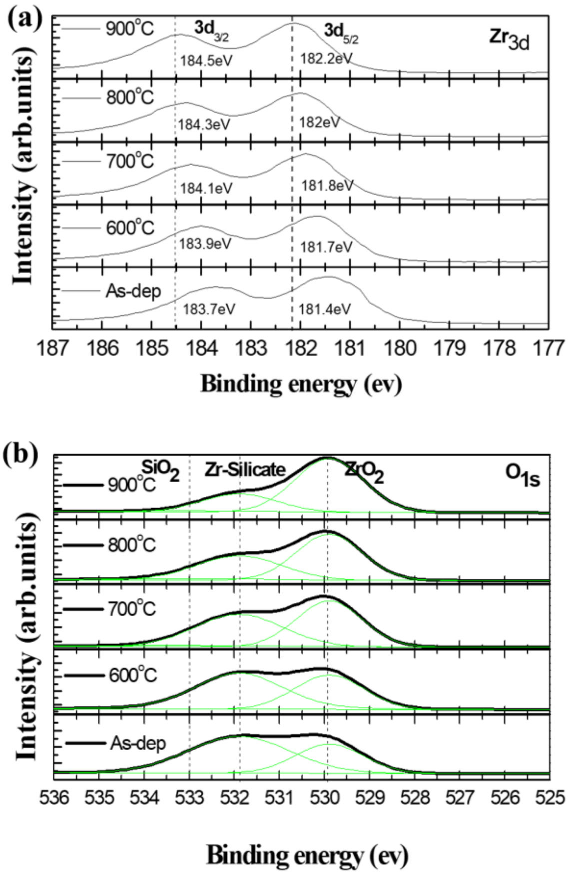


Fig.3 XPS results of (a)Zr 3d, (b)O 1s in ZrO_2 film after annealing at various temperatures in O_2 ambient

To investigate the effect of RTA annealing temperature to ZrO_2 sensing film, the AFM was used to analysis. Fig.4(a)-(e) showed the atomic force microscopy (AFM) images of the ZrO_2 films. The root mean square (rms) values of the above five samples for as-dep and RTA annealing from 600ºC to 900ºC were 3.08nm, 3.56nm, 4.04nm, 4.46nm, 5.48nm. The PZT films annealed at 900°C distinctly had the highest root mean square surface roughness (R_{ms}) 31.9nm. These results of AFM also echo the measurement results of XRD and XPS. The oxygen can effectively combine with zirconium atoms to form larger grains.

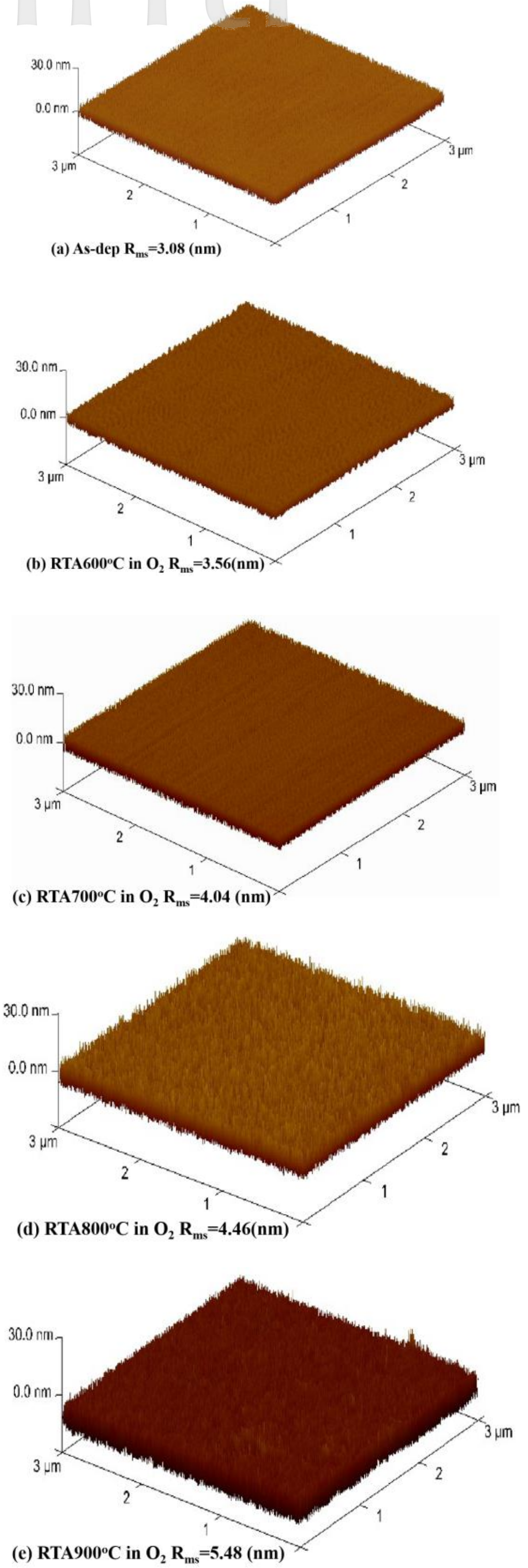
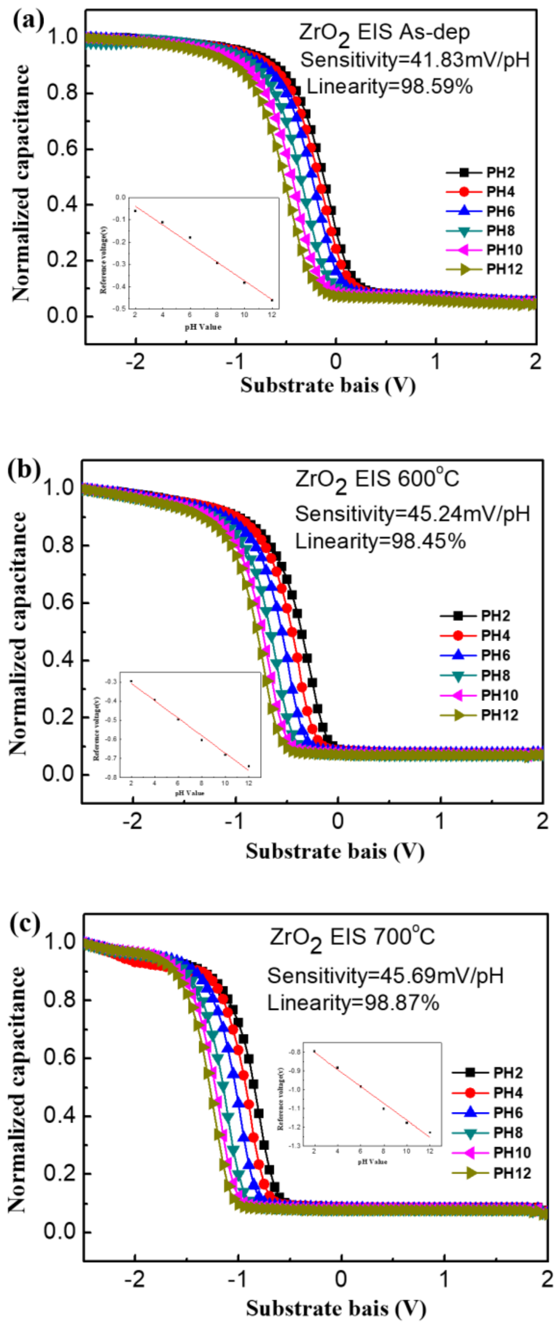


Fig.4 AFM of high-k ZrO_2 surface on single crystalline silicon after RTA at different temperatures in O_2 ambient for 30s.

Fig.5 showed the C-V curves of control and 600 °C to 900°C RTA annealed ZrO_2 film immersed in buffer solution with various pH values. The threshold voltage shift of the ZrO_2 membrane annealed at 900°C versus pH value of the solution reveals that the sensitivity of the device was as high as 51.84mV/pH.



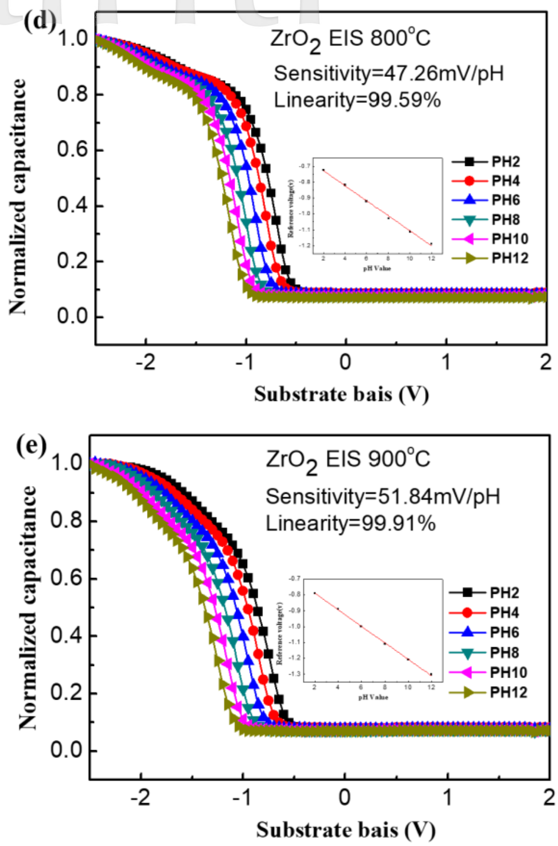


Fig.5 The normalized C-V curve of the ZrO_2 sample without and with RTA600 to 900℃ annealing in O_2. The inset figure represents the sensitivity and linearity

Compare of the as-deposited sample and the sample annealed at 600 and 900ºC of the sensitivity were 41.83, 45.24, 45.69, 47.26 and 51.84mV/pH, respectively. The sample annealed in the temperature of 900ºC possessed the highest sensitivity and linearity shown in Fig. 6.

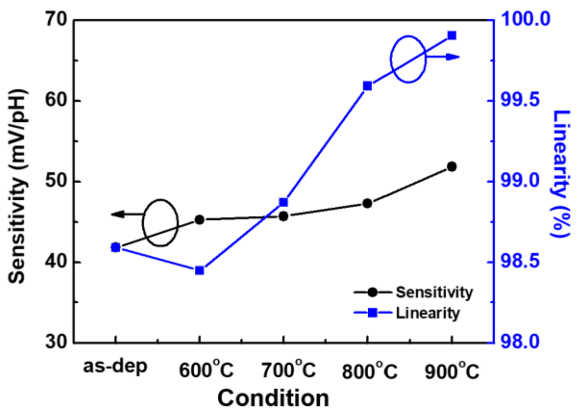


Fig.6 The sample with different RTA temperature in O_2 ambient.

Besides, Fig.7 shows that the hysteresis voltage of the as-deposited sample and the RTA annealed samples from 600, 700, 800 and 900ºC is 19.64, 13.79, 11.24, 8.04, and 6.56mV. The sample annealed at 900ºC had the lowest hysteresis deviation. Since the dangling bonds and defects of the membrane might cause attachments of ions, which suppressed diffusion of reacting ions and delayed the reference voltage response [10].

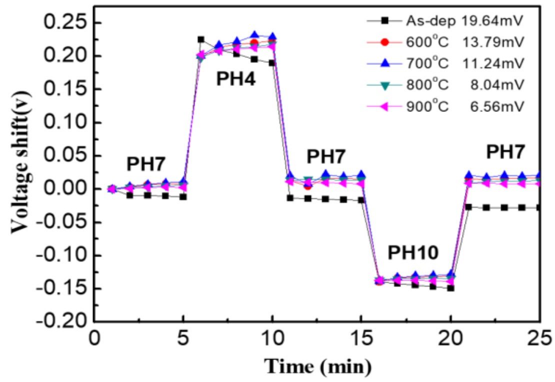


Fig.7 The hysteresis of ZrO_2 sensing membrane at various RTA temperatures.

Furthermore, Fig.8 shows the drift rate of the as-deposited sample and the sample annealed at 600, 700, 800, and 900ºC were 13.11, 11.79, 9.41, 7.32 and 4.82mV/hr, respectively. It can be seen the ZrO_2 sensing membrane with 900ºC annealing has lower hysteresis voltage and drift rate than other samples in Fig.9.

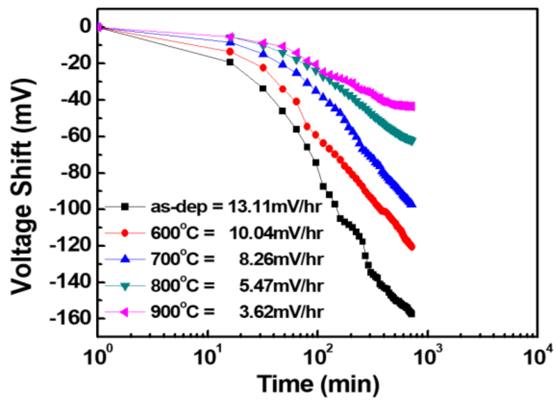


Fig.8 The drift voltage of ZrO_2 sensing membrane at various RTA temperatures.

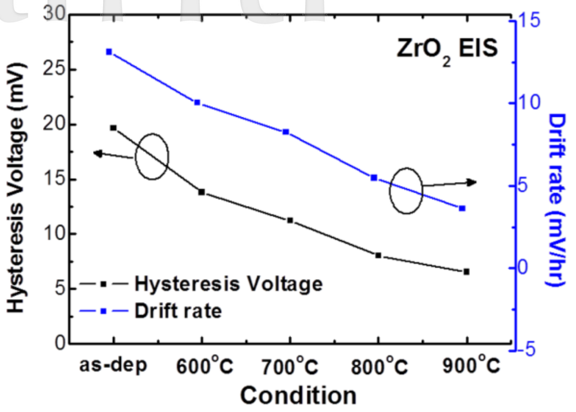


Fig.9 The hysteresis and drift rate at various RTA temperatures.

The comparison of ZrO_2 sensing membranes annealed with various RTA temperatures in O_2 ambient for sensitivity, linearity, hysteresis voltage, and drift rate was shown in Table-1.

	As-dep	600°C	700°C	800°C	900°C
Sensitivity (mV/pH)	41.83	45.24	45.69	47.26	51.84
Hysteresis voltage (mV)	19.64	13.79	11.24	8.04	6.56
Drift rate (mV/hr)	13.11	10.04	8.26	5.47	3.62

Table-1 the sensing performance of ZrO_2 sensing membrane annealed with various RTA temperatures in O_2 ambient

Otherwise, we also prepared the sodium and potassium ions solution, the concentration was controlled in a range between 10^{-5}M and 10^{-1}M. The calculated pNa and pK sensitivity of ZrO_2 sensing membrane annealed in O_2 were shown in Fig.8. The pNa and pK sensitivity of ZrO_2 sensing membrane with post-RTA are 7.07mV/pNa and 5.58mV/pK, respectively. It is evident that the ZrO_2 sensing membrane in EIS has more sensitive to H^+ relative to Na^+ and K^+.

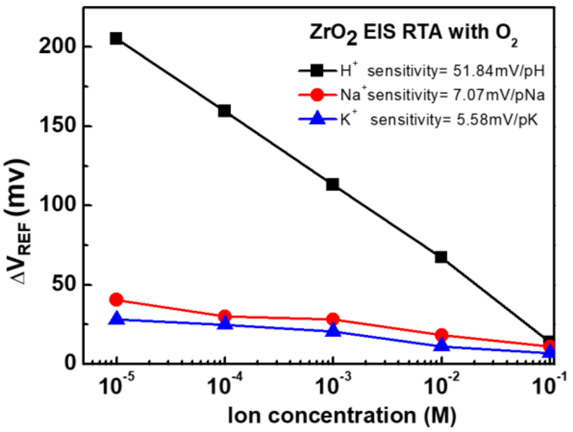


Fig.8 The different ion sensitivity of ZrO_2 sensing membrane annealed 900°C in O_2 ambient.

4. Conclusions

In this study, the ZrO_2 sensing membrane annealed at 900°C in O_2 ambient shows a higher sensitivity, higher linearity, higher H^+, Na^+, K^+ selectivity, lower hysteresis voltage and lower drift rate than other conditions. It can be confirmed, the ZrO_2 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. The ZrO_2 sensing film annealed at 900°C in O_2 ambient applied in sodium and potassium ions solution (K^+ and Na^+) biosensor shows higher sensitivity and linearity. This result demonstrated that the ZrO_2 sensing membrane on the EIS structure is ideal for biomedical device applications.

References

1. L. Bousse, S. Mostarshed, B. Van der Schoot and N. F. de Rooij, Comparison of the hysteresis of Ta_2O_5 and Si_3N_4 pH-sensing insulators, Sensors and Actuators B, 17 (1994) 157-164.
2. Hock Jin Quah, Kuan Yew Cheong“ Effects of post-deposition annealing ambient on Y_2O_3 gate

deposited on silicon by RF magnetron sputtering" Journal of Alloys and Compounds 529 73-83(2012)

3. T. Schroeder, G. Lupina, J. Dabrowski, A. Mane, Ch. Wenger, G. Lippert, H.J. Mussig, "Titanium-added praseodymium silicate high-k layers on Si(0 0 1) ", Appl. Phys. Lett. 87 022902. (2005)

4. S. Jeon, H. Hwang, "Electrical and physical characteristics of $PrTi_xO_y$ for metal oxide semiconductor gate dielectric applications", Appl. Phys. Lett. 81 (2002)4856-4858.

5. C.Y. Chen, J.C. Chou, H.T. Chou, "Characteristics of cost-effective ultrathin $HfTiO_x$ film as sensitive membrane in ISFET fabricated by anodization" J. Electrochem. Soc. 156 H225－H228. (2009)

6. M. Fanciulli, G. Scarel, Rare Earth Oxide Thin Film: "Growth, Characterization, and Applications" Springer, Berlin, 2007 Tung-Ming Pan, APL 87 262908 (2005)

7. L. Bousse, S. Mostarshed, B. van der Schoot, N.F. de Rooij, "Comparison of the hysteresis of Ta_2O_5 and Si_3N_4 pH-sensing insulators, "Sens. Actuator B 17 157-164. (1994)

8. L. Bousse, H.H. van den Vlekkert, N.F. de Rooij, "Hysteresis in Al_2O_3-gate ISFETs" Sens. Actuator B 2 103－110. (1990)

9. S.P. Pogorelova, A.B. Kharitonov, I. Willner, C.N. Sukenik, H. Pizem, T. Bayer, "Development of ion-sensitive field-effect transistor-based sensors for benzyl phosphoric acids and thiophenols using molecularly imprinted TiO_2 films" Anal. Chim. Acta 504 (2004) 113-122.

10. Luc Bousse, H.H. Van Den and N.F. De Rooij, "Hysteresis in Al_2O_3-gate ISFETs", Sensors and Actuators B, 2 (1990) 103-110

11. SH.D. Kim, S.-W. Jeong, M.T. "Effects of annealing gas (N_2, N_2O, O_2) on the characteristics of $ZrSi_xO_y/ZrO_2$ high-k gate oxide in MOS devices" Thin Solid Films 515 522-525 (2006)

12. Hao-Chun Chuang, Tseng-Fu Lu,"Thickness effect and rapid thermal annealing treatment of single atomic layer deposition HfO_2 layer on EIS for pH sensor application". INEC conference (2010)

13. Haslinda Abdul Hamid, Mat Johar Abdullah, "Effect of N_2 and 0_2 Anneal Gas Ratio For Low Resistance p-Type ZnO Formation. Kuala Lumpur, Malaysia ICSE(2006)

14. Dail Eom, Sang Yong No, Cheol Seong Hwang, "Deposition Characteristics and Annealing Effect of La_2O_3 Films Prepared Using $La(iPrCp)_3$ Precursor" Journal of The Electrochemical Society, 154 (3) G49-G53 (2007)

15. Mindaugas ANDRULEVICIUS, "XPS Investigation of TiO_2 / ZrO_2/ SiO_2 Films Modified with Ag/Au Nano particles," ISSN 1392-1320 MATERIALS SCIENCE (MEDZIAGOTYRA). Vol. 14, No. 1. (2008)

16. j. zhu, z.g. liu, "Thermal stability and electrical properties of Zr silicate films for high-k gate-dielectric applications, as prepared by pulsed laser deposition" Apply. Phys. A 80, 321–324 (2005)

17. D.Sotiropoulou, "An XPS and XAES study of the Ni/ZrO_2 interface" Surface Science 408182–189 (1998)