Oxygen annealed ZnO–La$_2$O$_3$ TFTs fabricated using CBD technique

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Abstract. Cost-effective chemical bath deposition (CBD) technique have been utilized to fabricate ZnO thin films on ultrasonically cleaned glass substrates and successfully applied as channel layer in thin film transistors (TFTs). The deposited films are characterized by XRD and SEM analysis. High-k rare earth oxide La$_2$O$_3$ is used as gate dielectric. The ZnO films are annealed at ambient and oxygen atmosphere at 500°C for one hour. The I-V characteristics of the TFTs are studied and various electrical parameters such as field effect mobility, threshold voltage, sub-threshold swing, drain current ON/OFF ratio and transconductance are evaluated.

1. Introduction
Due to the wide band gap (3.37 eV) and high excitation binding energy (60 meV), ZnO is a strong candidate as semiconductor material in recent years in various electronics devices such as solar cell windows, gas sensors, light emitting diodes, TFTs etc. [1]. ZnO received significant attention especially in TFTs because of its high temperature performance, optical transparency, excellent electrical conductivity and non-toxic properties [2]. The light degradation and opaqueness of silicon limits its applications in modern optoelectronics [3, 4]. But it has been reported that the metal oxide semiconductor ZnO does not interact with visible light due to its wide band gap and hence TFTs based on ZnO are widely used in display technologies [3, 4]. Also, ZnO TFTs exhibit higher mobility than those of Si and organic TFTs. Organic TFTs also have the limitation of environment degradation [5]. In contrast, ZnO offers high transparency, high field effect mobility, high uniformity, high environmental stability, less light sensitivity and excellent mechanical, chemical and electrical stabilities and permits to operate at much higher voltage and hence received significant attention as an alternative to conventional Si and organic semiconductors in the recent years [5-8]. Out of the various techniques, non-vacuum processes such as chemical or wet processes that include chemical vapor deposition, chemical bath deposition, sol-gel method etc. are preferable for fabrication of simple, cost effective and easy scalability ZnO thin films [9]. In CBD technique, an aqueous solution made up of some mixture of precursor solution and complexing agents and substrates are required for the deposition of thin films. CBD technique has the advantage of low temperature processing, large area substrates fabrication and reproducibility [10, 11].

The rare earth oxides such as La$_2$O$_3$, Nd$_2$O$_3$, Dy$_2$O$_3$ etc. are successfully applied as gate dielectric material in electronic devices due to their high dielectric constant, high thermal and chemical stabilities [12-15]. Out of the various rare earth oxides, the La$_2$O$_3$ has high dielectric constant (14.77) [16] and low leakage current [12, 17] which is suitable for replacing conventional SiO$_2$ in TFTs. It has
been reported that La$_2$O$_3$ is a successful candidate as gate dielectric in TFTs and microelectronics [14, 15, 18-22]. In this report we have investigated the electrical characteristics of ZnO- La$_2$O$_3$ TFTs fabricated using ZnO thin films as active material prepared by CBD technique, reported earlier [23] and evaluated various electrical parameters of the TFTs annealed at oxygen atmosphere. The ZnO thin films are characterized by XRD and SEM analysis.

2. Experimental details

The TFTs are prepared using CBD technique on ultrasonically cleaned glass substrates. First 100 ml of 0.1 M ZnCl$_2$ aqueous solution is prepared using deionized water and then NaOH is added into the ZnCl$_2$ solution to prepare Na$_2$ZnO$_2$ bath. The mixer is then stirred in a magnetic stirrer for 30 minutes. Initially a white precipitate of Zn(OH)$_2$ is formed. A clear solution is obtained after addition of 60 ml of 4 M NaOH solution into the bath. The mixer is again stirred for 30 minutes. In the entire process the bath temperature is maintained at 40°C. The pH of the solution is 11. The chemical reactions are as follows:

\[
\text{ZnCl}_2 + 2\text{NaOH} = \text{Zn(OH)}_2 + 2\text{NaCl}
\]

\[
\text{Zn(OH)}_2 + 2\text{NaOH} = \text{Na}_2\text{ZnO}_2 + 2\text{H}_2\text{O}
\]

The ZnO thin films are deposited on the substrates by alternate dipping into the (Na$_2$ZnO$_2$) bath and then into hot water bath. This leads to the reaction

\[
\text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O} = \text{ZnO} + \text{NaOH}
\]

Zinc hydroxide is formed due to hydrolysis of deposited ZnO during subsequent immersions in hot water. The film thickness can be increased by increasing the immersion frequency into the bath. In this investigation the number of immersions is 20-25 and the immersion time is 5 seconds into the two baths for deposition of each ZnO films. Some films are annealed at 500°C for 1 hour in air and some are annealed in oxygen atmosphere at same temperature and time and uniform transparent films of ZnO are obtained.

3. Results and discussion

Figures 1 (a) and (b) show the XRD patterns of ZnO thin films annealed at 500°C in ambient and oxygen atmosphere respectively. Eight distinct and sharp peaks, viz. (100), (002), (101), (102), (110), (103), (112) and (201) of ZnO are observed in the XRD patterns of the ZnO films annealed in oxygen atmosphere at 500°C for one hour (figure 1 (b)). This confirms the typical hexagonal structure of ZnO according to JCPDS [23] and also of good polycrystalline growth of ZnO thin film fabricated by CBD technique. The XRD patterns of the ZnO films shown in figure 1 (b), obtained from the ZnO films annealed at ambient atmosphere at 500°C for one hour, show only three peaks, viz. (100), (002) and (101) that indicate comparatively poor polycrystalline growth of the films than that of the films annealed at oxygen atmosphere.
Figures 2 (a) and (b) show the SEM images of the ZnO thin films annealed at ambient and oxygen atmosphere at 500°C, respectively. From the SEM analysis it is seen that the oxygen annealed sample shows comparatively uniform granular structure than the air annealed sample. The fabrication details of the TFTs is: Al source-drain electrodes are deposited over the ZnO film maintaining a channel of length 50 µm and channel width 0.1 cm. La$_2$O$_3$ is deposited over the source-drain electrodes as gate dielectric layer. Over the dielectric layer Al is again deposited as gate electrode. Figure 3 shows the coplanar electrode structure of the fabricated TFTs.

![Figure 1. XRD patterns annealed (a) at air atmosphere (b) oxygen atmosphere](image1)

![Figure 2. SEM image annealed (a) at air atmosphere (b) oxygen atmosphere](image2)

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![Figure 3. Coplanar electrode structure of the ZnO TFTs](image3)

The suitability of La$_2$O$_3$ as dielectric layer in the TFTs is tested by fabricating an Al/ La$_2$O$_3$/Al structure over a glass substrate by thermal deposition technique in high vacuum. From this structure the current density ($J$) vs. voltage ($V$) characteristics (figure 4) of the dielectric films are observed and find that La$_2$O$_3$ film shows very low leakage current which reveals the suitability of La$_2$O$_3$ as dielectric material in thin film transistors.

Figures 4 and 5 show $I$-$V$ characteristics of ZnO TFTs annealed at ambient and oxygen atmosphere at 500°C for one hour. Well-modulated and high drain current is observed in case of the TFTs.
annealed at oxygen atmosphere. Well saturated characteristics are also observed in case of oxygen annealed samples. The TFTs are operated in enhancement mode.

![Figure 4. J-V characteristics of Al/ La$_2$O$_3$/Al structure](image)

**Figure 4.** J-V characteristics of Al/ La$_2$O$_3$/Al structure

![Figure 5. I$_D$ - V$_D$ characteristics of ZnO TFTs annealed at ambient atmosphere](image)

**Figure 5.** I$_D$ - V$_D$ characteristics of ZnO TFTs annealed at ambient atmosphere

The field effect mobility of the TFTs are evaluated using equation (1)[24], which represent the expression for drain current in the saturation region ($V_D = V_G - V_T$).

$$I_{D_{Sat}} = \frac{W}{2L} \mu_{FE} C_f (V_G - V_T)^2,$$

where $W$ is the channel width, $L$ is channel length, $C_f$ is the gate capacitance per unit area, $V_T$ is the threshold voltage, $V_G$ is the gate voltage and $\mu_{FE}$ is the field-effect mobility. The field effect mobilities, threshold voltages, sub-threshold swing, drain current ON/OFF ratio and transconductance of the devices annealed at air and oxygen atmosphere are evaluated using theoretical model and values are presented in table 1.

The ($I_D$)$^{1/2}$ - $V_G$ plots for the TFTs at constant drain voltage $V_D = 10$ V are shown in figures 6 (a) and (b). Figure 6 (a) is for ambient annealed sample and figure (b) is for oxygen annealed sample. From the extrapolation of the linear portion of the graph to the $V_G$ axis (figure 6), the threshold voltages ($V_T$) of the devices are calculated and found to be 2.8V and 3.8 V, respectively, for air and oxygen annealed samples.
Figure 6. \((I_D)^{1/2}\) vs. \(V_G\) curve of the TFTs. Curve (a) annealed at ambient atmosphere Curve (b) annealed at oxygen atmosphere

The field-effect mobility \(\mu_{FE}\) is calculated from equation 1 and found to be 0.6 and 1.6 cm\(^2\)/VS respectively for air and oxygen annealed TFTs. The transfer characteristics \(\log(I_D)\) vs. \((V_G)\) at constant drain voltage \(V_D = 10\) V of the TFTs are shown in figure 7. In figure 7, curve (a) represents the air annealed sample and curve (b) represents the oxygen annealed sample. The drain current ON-OFF ratio of the devices is measured from figure 7 using equation (2) [24] and found to be \(10^6\) and \(10^7\) respectively for air and oxygen annealed samples.

\[
\frac{I_{ON}}{I_{OFF}} = \frac{C_i\mu_{FE}(V_G - V_T)^2}{\sigma d V_D}
\]  

(2)

where \(\sigma\) and \(d\) are conductivity and thickness of the semiconductor of the TFTs. The sub-threshold swing is calculated from the slope of the graphs using the equation (3) [25] and found as 1V/decade and 0.8V/decade for respective air and oxygen annealed samples.

\[
s = \left(\frac{\delta \log I_D}{\delta V_G}\right)^{-1}
\]

(3)

The high ON-OFF ratio of the devices is also due to the enhanced oxygen content in the ZnO films annealed at 500\(^\circ\) C in oxygen atmosphere, as the induced interface carrier concentration depends on the oxygen content in ZnO films [24].
Figure 7. The transfer characteristics log \( I_D \) vs. \( V_G \) at constant drain voltage \( V_D = 10 \) V. Curve (a) air annealed sample, curve (b) oxygen annealed sample

The transconductance \( g_m \) of the device is evaluated from the equation (4) [26] as

\[
g_m = \frac{\partial I_D}{\partial V_G} \bigg|_{V_D=\text{const}} = \mu_{FE} C_i \frac{V_D}{L^2}
\]

The transconductance of the air and oxygen annealed samples are found to be \( 0.2 \times 10^{-3} \) mho and \( 1 \times 10^{-3} \) mho respectively.

Table 1 contains the values of field effect mobility, threshold voltage, sub-threshold swing, drain current ON/OFF ratio and transconductance of the devices annealed at ambient and oxygen atmosphere. From the table 1 it can be concluded that the oxygen annealed TFTs exhibit comparatively improved values of electrical parameters than that of air annealed TFTs. The field effect mobility of oxygen annealed TFTs found to be high and the threshold voltage and sub-threshold swing of oxygen annealed TFTs are found to be relatively low. The improved value of the field effect mobility of the oxygen annealed TFT is due to the reduction of structural defect of the ZnO crystal as the films are annealed in oxygen atmosphere at \( 500^\circ \) C [27]. The oxygen atoms passivated into the
interstitial positions of the ZnO crystals while annealing in oxygen atmosphere at 500°C for one hour and reduces the trapping of charges in the grain boundaries. Consequently, the potential barrier at the grain boundaries are reduced. The number of shallow donors of interstitial Zn atoms also decreases due to the annealing at oxygen atmosphere and increases the mobility of the carriers [21, 27].

4. Conclusions
Finally, it can be concluded that the ZnO TFTs fabricated using CBD exhibits improved electrical properties when annealed in oxygen atmosphere at 500°C. High field effect mobility, high drain current ON-OFF ratio, low threshold voltage, sub-threshold swing and high transconductance have been observed in the case of the oxygen annealed TFTs.

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