1. Introduction

Nowadays, metal-oxide (MO) thin film transistors (TFTs) have attracted widespread attention in many fields, such as flat panel displays (FPDs), because of their excellent electrical performance, high transparency, good uniformity and compatibility with a variety of preparation processes.\(^1\)\(^-\)\(^4\) One of the most important parts in thin film transistors is the dielectric layer, which can insulate the semiconductor from the gate electrode, so that the carriers can be controllably aggregated in a semiconductor. Recently, research on metal-oxide dielectrics with high dielectric constants (high-\(k\)) (e.g., ZrO\(_2\), Al\(_2\)O\(_3\), HfO\(_2\) (ref. 7) and Y\(_2\)O\(_3\) (ref. 8)) has been widely carried out, and some researchers have explored the application of metal oxide dielectrics in TFT devices. ZrO\(_2\) has a high dielectric constant (~25), high melting point (4300 °C), high refractive index and wide bandgap (~6 eV).\(^5\)\(^-\)\(^10\) Due to these excellent physical properties, ZrO\(_2\) has been regarded as one of the ideal metal-oxide dielectrics with low leakage current density.

Solution phase method (e.g., inkjet printing, spray coating and spin coating) is considered to be a novel approach to manufacturing high-quality MO\(_x\) films with low cost, and in this paper ZrO\(_2\) films were fabricated by spin coating under ambient conditions. Thermal annealing, with the intention of removing impurities and decreasing the concentration of defect states, is regarded as a necessary process for high quality solution-processed films. Usually, the spin coating process is repeated several times to achieve the desired thickness and reduce pores and defects. After each spin coating, the wet film is briefly annealed, which is called pre-annealing process. And then, after deposition of the final layer, multi-layer films are annealed for a longer time, which is defined as post-annealing. Pre-annealing temperature is lower aiming to evaporating the solvent, while the higher post-annealing temperature plays an important role in promoting metal-oxide bond formation and reducing impurity.\(^11\) Several studies have been carried out to investigate the effect of thermal annealing on metal oxide film.\(^12\)\(^-\)\(^14\) However, the effect of pre-annealing temperature and post-annealing temperature was not systematically discussed in these reports. The pre-annealing process and post-annealing process can be associated with different reactions, and therefore a targeted, systematic analysis of their effects should be performed. In this paper, ZrO\(_2\) dielectrics were deposited by solution method with varying pre-annealing temperatures and post-annealing temperatures. The thermal effect of pre-annealing and post-annealing process on the structural and electrical properties...
of ZrO$_2$ film was investigated. In particular, the effect of pre-annealing temperature on solvent evaporation and internal stress was discussed, while the effect of post-annealing temperature on the internal impurities and interface defects was also evaluated.

2. Results and discussion

Usually, a sol–gel process consists of two steps, hydrolysis and condensation.$^{1,2}$ In order to explore the hydrolysis and condensation process, and choose the annealing temperature, the thermal gravimetric and differential scanning calorimetry (TGA-DSC) analysis was carried out. Fig. 1(a) is the TG-DSC result of ZrO$_2$ precursor. The endothermic reactions at 99.7 °C and 136.5 °C indicated hydrolysis of the ZrO$_2$ solution and solvent evaporation. There was no significant weight change after 150 °C, corresponding to the boiling point of the 2-MOE solvent. The exothermic peak at 155.0 °C indicated the formation of metal–oxygen–metal (M–O–M) framework. The endothermic peak at 175.5 °C was associated with the reduction of impurities, while the exothermic peaks (at 335.6, 443.5 and 671.6 °C) can be attributed to the crystallization.

To further analyse the thermal behaviour of ZrO$_2$ precursor, the Fourier Transform Infrared (FTIR) analysis was carried out with ZrO$_2$ precursor annealed at different temperatures (room temperature (RT), 60, 90, 120 and 150 °C). As shown in Fig. 1(b), the absorption peak located at 3000–3800 cm$^{-1}$ represents the stretching vibration of –OH bonding, which was derived from the absorption of oxygen in the air to form an –OH group. The peak located at 1600 cm$^{-1}$ can be associated with the O–C–O group, which was mainly derived from the residual solvent. It can be seen that when the annealing temperature reached 150 °C, no O–C–O group was detected, indicating that the solvent was substantially removed. The absorption peak at 1470–1360 cm$^{-1}$ and 1250–1030 cm$^{-1}$ were caused by the bending vibration of carbon–hydrogen bond and bending vibration of carbon–oxygen bond, respectively. Finally, the absorption peak at 500 cm$^{-1}$ can be attributed to the Zr–O group.

Fig. 1 (a) The TG-DSC result of ZrO$_2$ precursor at a heating rate of 10 °C min$^{-1}$. (b) The FTIR spectra of ZrO$_2$ precursor annealed at different temperatures.

Based on the discussion above, an annealing temperature higher than 136 °C is necessary for the removal of solvent, while above 155 °C is important for promoting metal-oxide bond formation. In addition, a crystalline ZrO$_2$ film can be obtained with an annealing temperature higher than 350 °C. In order to investigate the effect of pre-annealing temperature and post-annealing temperature on the properties of ZrO$_2$ films, a series of experiments were carried out.

2.1 The effect of pre-annealing temperature

The ZrO$_2$ film was deposited by spin-coating at 5000 rpm for 40 s and the spin-coating process was repeated 3 times. The pre-annealing temperature was set to 100, 200, 300 and 400 °C (for 5 min), and the post-annealing temperature was set to 450 °C. These films were labelled as 100-Zr, 200-Zr, 300-Zr and 400-Zr, respectively. A high post-annealing temperature could facilitate crystallization, which is advantageous for analysing the internal stress of ZrO$_2$ films. The thickness and density of ZrO$_2$ films with different pre-annealing temperatures were measured by XRR, as shown in Fig. 2(a). Based on the measured density, the relative porosity volume (R) of ZrO$_2$ film was calculated by the following formula.$^{16}$

$$R = \frac{\rho_1 - \rho}{\rho_1 - \rho_h}$$

(1)

Fig. 2 (a) The XRR result of ZrO$_2$ films with different pre-annealing temperatures. (b) XRD spectra the ZrO$_2$ films at different pre-annealing temperatures.
$\rho_1$ and $\rho$ represent the theoretical density of bulk ZrO$_2$ materials (5.68 g cm$^{-3}$) and the film density measured by XRR, respectively. $\rho_h$ is the hole density (air), and in this case it is approximately zero. The detailed data of XRR result is listed in Table 1.

Fig. 2(b) is XRD spectra of ZrO$_2$ films with different pre-annealing temperatures. All diffraction patterns shown characteristic ZrO$_2$ peaks with both tetragonal structure and monoclinic structure [JCPDS#79-1771 and JCPDS#78-0047]. The diffraction peaks located at 30.3°, 50.4°, and 60.3° can be associated with (101), (112), and (211) crystal faces, respectively. Usually, internal stress will be formed in the laminated device. In this paper, the stress of ZrO$_2$ which deteriorates the quality of the laminated device is evaluated by the following formula.

$$D = \frac{0.9\lambda}{(\beta \cos \theta)}$$ 

(2)

$\lambda$ is the X-ray wavelength (0.154 056 nm), while $\beta$ and $\theta$ are the full width at half maximum (FWHM) and Bragg’s angle, respectively. Usually, internal stress will be formed in the film due to the change of temperature during annealing process, which deteriorates the quality of the film and the stability of the laminated device. In this paper, the stress of ZrO$_2$ films is evaluated by calculating the microstrain. The microstrain ($\varepsilon$) of ZrO$_2$ films with different pre-annealing temperatures can be investigated by the following formula.

$$\varepsilon = \frac{1}{\sin \theta} \left[ \frac{\lambda}{D} \right] - (\beta \cos \theta)$$ 

(3)

The structural parameters of ZrO$_2$ films with different pre-annealing temperatures are listed in Table 1, and their trends are shown in Fig. 3. It was found that the ZrO$_2$ film with pre-annealing temperature of 200°C shown the optimal property, with the lowest average microstrain and the highest density. Typically, the purpose of the pre-annealing process is to remove the solvent and improve the quality of the subsequent film. When the pre-annealing temperature is too low, the solvent could not be completely removed. The residual solvent is covered by the subsequent film, leading to large roughness and low density. As a result, the ZrO$_2$ film with pre-annealing temperature of 100°C had the lowest density and the largest relative porosity. However, the solvent evaporates rapidly at a too high pre-annealing temperature, such as 300 and 400°C, which also increases the porosity and reduces the density. In addition, the rapid evaporation of solvent also leads to greater residual stress, so the ZrO$_2$ films with pre-annealing temperatures of 300 and 400°C exhibited a large average microstrain. As the pre-annealing temperature increased from 100°C to 400°C, the intensity of the (111) crystal plane decreased first, reaching a minimum at 200°C, and then it had a recovery. Since the XRD diffraction intensity was related to the content, ZrO$_2$ film with pre-annealing temperature of 200°C contained the lowest amount of monoclinic structure phase, showing a purer structure.

### Table 1 Structural parameters of ZrO$_2$ films with different pre-annealing temperature

| Sample name | Thickness (nm) | Density (g cm$^{-3}$) | Relative porosity (volume %) | hkl | $2\theta$ (deg) | FWHM (deg) | $d$ (Å) | $D$ (nm) | $\varepsilon$ (%) | Average $D$ (nm) | Average $\varepsilon$ (%) |
|-------------|---------------|----------------------|-----------------------------|-----|----------------|------------|--------|--------|--------------|----------------|-------------------|
| 100-Zr      | 84.37         | 5.12                 | 9.93                        | 101 | 30.39         | 0.41       | 2.94   | 19.70  | 0.33         | 19.79           | 0.25              |
|             |               |                      |                             | 111 | 31.57         | 0.35       | 2.83   | 23.05  | 0.27         |                 |                   |
|             |               |                      |                             | 112 | 50.53         | 0.41       | 1.81   | 21.02  | 0.19         |                 |                   |
|             |               |                      |                             | 211 | 60.33         | 0.59       | 1.53   | 15.39  | 0.22         |                 |                   |
| 200-Zr      | 81.87         | 5.45                 | 4.03                        | 101 | 30.39         | 0.41       | 2.94   | 19.70  | 0.33         | 22.98           | 0.23              |
|             |               |                      |                             | 111 | 30.55         | 0.35       | 2.84   | 23.05  | 0.27         |                 |                   |
|             |               |                      |                             | 112 | 50.56         | 0.47       | 1.81   | 18.38  | 0.22         |                 |                   |
|             |               |                      |                             | 211 | 60.33         | 0.30       | 1.53   | 30.78  | 0.11         |                 |                   |
| 300-Zr      | 84.47         | 5.20                 | 8.45                        | 101 | 30.41         | 0.41       | 2.94   | 19.70  | 0.33         | 18.65           | 0.27              |
|             |               |                      |                             | 111 | 31.62         | 0.47       | 2.83   | 17.29  | 0.36         |                 |                   |
|             |               |                      |                             | 112 | 50.44         | 0.47       | 1.81   | 18.39  | 0.22         |                 |                   |
|             |               |                      |                             | 211 | 60.38         | 0.47       | 1.53   | 19.24  | 0.18         |                 |                   |
| 400-Zr      | 85.00         | 5.20                 | 8.45                        | 101 | 30.51         | 0.41       | 2.93   | 19.70  | 0.33         | 18.77           | 0.26              |
|             |               |                      |                             | 111 | 31.63         | 0.41       | 2.83   | 19.76  | 0.31         |                 |                   |
|             |               |                      |                             | 112 | 50.64         | 0.53       | 1.80   | 16.35  | 0.24         |                 |                   |
|             |               |                      |                             | 211 | 60.46         | 0.47       | 1.53   | 19.25  | 0.17         |                 |                   |
Based on the discussion above, the optimal pre-annealing was used to describe the surface morphology of ZrO$_2$. The annealing temperature was set to 200, 250, 300 and 400 °C for 1 hour. These films were labelled as Zr-200, Zr-250, Zr-300 and Zr-400, respectively. Fig. 5 is XRR and XRD spectra of ZrO$_2$ films with different post-annealing temperatures. The crystallization of ZrO$_2$ films annealed at different temperatures was measured by XRD, as shown in Fig. 5(b). Except for the ZrO$_2$ film post-annealed at 400 °C, the ZrO$_2$ films annealed at the other three temperatures were amorphous, which was consistent with the TG-DSC result. The diffraction peaks located at 30.3°, 50.7°, and 60.2° can be associated with (101), (112), and (211) crystal faces, respectively [tetragonal structure, JCPDS#779-1771].

Fig. 6 shows the XPS results of the ZrO$_2$ films with different post-annealing temperatures. As shown in Fig. 6(a), the Zr 3d$_{5/2}$ peak located at 182.7 eV represented the metal–oxygen–metal (M–O–M) components while the Zr 3d$_{3/2}$ peak located at 185.1 eV indicated the spin–orbit component. A shift to lower binding energies was observed when the post-annealing temperature increased, which can be associated with the oxidation behaviour from Zr(NO$_3$)$_4$ to ZrO$_2$. In Fig. 6(b–e), the oxygen 1s peak can be divided into three peak components. The peaks located at 530.0 eV, 531.5 eV and 532.8 eV can be associated with M–O–M component, M–OH component and M–NO$_3$ component, respectively. The M–O–M component indicates the formation of metal–oxygen–metal framework. The M–OH component was derived from the hydrolysis reaction between Zr$^4+$ ion and 2-MOE, and the M–NO$_3$ component can be attributed to the residual Zr(NO$_3$)$_4$ solute. Both of the M–OH component and M–NO$_3$ component are associated with defect states in ZrO$_2$ films. These impurity components will introduce defect levels into the forbidden band, thus declining the dielectric properties of the ZrO$_2$ film. As the post-annealing temperature increased, both M–OH component and M–NO$_3$ component decreased. When the post-annealing temperature
up to 300 °C, M–NO₃ component in the film was almost completely removed, which was consistent with N 1s spectra of ZrO₂ films with different post-annealing temperatures (ESI Table 1†).

Table 2 is the structural parameters of ZrO₂ films with different post-annealing temperatures, and the trend of these parameters is shown in Fig. 7. It was found that the thickness of ZrO₂ film decreased rapidly as the post-annealing temperature increased from 200 to 300 °C. Since then it flattened off at a level of around 84 nm. Due to the evaporation of solvent and the decomposition of impurity, ZrO₂ films prepared by solution-phase method may have many pores and defects. Therefore, high temperature heat treatment is required to promote atom rearrangement, thereby forming a denser film. As the post-annealing temperature increased, the density of ZrO₂ films increased and the relative porosity volume decreased, which meant that a high post-annealing temperature is advantageous for obtaining a dense film. The percentage of M–O–M component increased with increasing post-annealing temperature, which was associated with the removal of impurities and orderly arrangement of atoms under high temperature.

The dielectric performance of ZrO₂ films with different post-annealing temperatures were measured by using an ITO/ZrO₂/Al capacitor. As shown in Fig. 8, the films post-annealed at 200 °C and 250 °C showed the largest leakage current density due to high concentration of defect states. The ZrO₂ films post-annealed at 300 °C and 400 °C exhibited excellent dielectric properties, with a leakage current density of 3.27 × 10⁻⁶ A cm⁻² and 2.261 × 10⁻⁶ A cm⁻² at 1 MV cm⁻¹, respectively. For the capacitance–voltage curve, the capacitance density of ZrO₂ films post-annealed at 200 °C and 250 °C gradually decrease to around zero due to the large leakage current. And the capacitance density of ZrO₂ films post-annealed at 300 °C and 400 °C hardly changed with voltage, exhibiting excellent dielectric properties. The ZrO₂ film post-annealed at 300 °C had a capacitance density of 320 nF cm⁻² and a dielectric constant (k) of 19, while the 400 °C annealed ZrO₂ film showed a capacitance density of 500 nF cm⁻² and a higher dielectric constant (k) of 30.

Based on the ZrO₂ films with different post-annealing temperatures, bottom-gate top-contact IGZO/ZrO₂ TFTs were fabricated, as shown in Fig. 9. The solution-processed ZrO₂ films were deposited on the ITO/glass substrate. The IGZO films were produced by RF magnetron sputtering with a pressure of 5 mTorr (O₂ : Ar = 5%) and then annealed at 200 °C for 1 hour. The atomic ratio composition of the IGZO target is In : Ga : Zn : O = 1 : 1 : 1 : 4. Finally, aluminium electrodes with a thickness of 100 nm were fabricated above IGZO films by direct current (DC) sputtering a pressure of 1 mTorr (O₂ : Ar = 0%).

Most of previous reports only discussed the effect of thermal annealing on the electrical properties of dielectric layer, and the effect on the interface between dielectric layer and...
Fig. 10 The μ-PCD mapping result of IGZO-TFT with ZrO₂ films under different post-annealing temperatures. (a) 200 °C, (b) 250 °C, (c) 300 °C and (d) 400 °C. (e) The μ-PCD decay curve of IGZO/ZrO₂ stack with ZrO₂ films under different post-annealing temperatures.

3. Experimental

The ZrO₂ solution was synthesized by dissolving 0.5 M zirconium nitrate pentahydrate [Zr(NO₃)₄·5H₂O] in 2-methoxyethanol, and then the solution was stirred vigorously for 24...
hour and then were aged for 48 hour under ambient conditions. The thermovimetric behaviour of the ZrO₂ precursor was measured by thermogravimetric differential scanning calorimetry (TG-DSC) and the heating rate was 10 °C min⁻¹. Fourier Transform infrared spectroscopy.

The crystallization of ZrO₂ films was measured by X-ray diffraction (XRD) (EMPYREAN, PANalytical, Almelo, The Netherlands). X-ray reflectivity (XRR) (The instrument is the same as XRD) was used to investigate the thicknesses and densities of ZrO₂ films. The chemical composition of ZrO₂ films was obtained by X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific, Waltham, MA, USA), and all peaks were calibrated by using the carbon 1s peak (284.8 eV) as a reference. Atomic force microscopy (AFM) (BY3000, Being Nano-Instruments, Beijing, China) was used to investigate the surface morphology of ZrO₂ films. Metal insulator metal (MIM) capacitors were fabricated by sputtering circular aluminium electrodes with a thickness of 100 nm on the ZrO₂ films, and Keithley4200 (Tektronix, Beaverton, Oregon, OR, USA) parameter analyser was used to investigate the electrical characteristics of MIM capacitors in air. IGZO film was fabricated by RF magnetron sputtering above ZrO₂ film. The decay curve and mapping result of IGZO/ZrO₂ stack was measured by μ-wave photo conductivity decay (μ-PCD) measurement system (KOBELECO, LTA-1620SP, Kobe, Japan).

The semiconductor parameter analyser (Agilent4155C, Agilent, Santa Clara, CA, USA) was used to investigate the output and transfer curves of TFTs in air. The field-effect mobility (μ) and threshold voltage (V_th) can be measured according to the following eqn (1). The subthreshold swing (SS) was extracted by fitting the eqn (2):

\[ I_d = \frac{1}{2} \frac{W}{L} \mu C (V_g - V_{th})^2 \]

\[ SS = \frac{dV_g}{d\log I_d} \]

μ and C represent the field-effect mobility and dielectric layer capacitance. I_d, V_th, V_g and V_d are drain current, threshold voltage, drain voltage and gate voltage, respectively. The length (L) and width (W) of channel are 325 and 515 μm, respectively.

4. Conclusions

In this paper, the thermal effect of pre-annealing and post-annealing process on solution-processed ZrO₂ dielectric was discussed. The thermal effect of pre-annealing temperature was investigated by various analysis, such as XRD, XRR and AFM. It was found that the pre-annealing process had a significant effect on the density and internal stress of ZrO₂ film. The ZrO₂ film with pre-annealing temperature of 100 °C shown the largest relative porosity owing to the inefficient evaporation of the solvent. And ZrO₂ films with pre-annealing temperature of 300 °C and 400 °C suffer from great residual stress and large pores due to the rapid evaporation of solvent. As for the post-annealing temperature, the post-annealing process can not only improve the electrical properties of ZrO₂ dielectric, but also optimize the interface between semiconductor and dielectric. As a result, the TFT with a pre-annealing temperature of 200 °C and a post-annealing temperature of 400 °C showed the best electrical performance, with a mobility of 16.34 cm² (V s)⁻¹ and an \( I_{on}/I_{off} \) of 2.08 × 10⁶.

Conflicts of interest

There are no conflicts to declare.

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