A dielectric material with a dielectric constant higher than that of thermally grown silicon dioxide (SiO₂) is required for the sub-100 nm metal-oxide-semiconductor field-effect transistor (MOSFET) to improve the device driving capability and suppress short channel effect (SCE). It is generally believed that the ultimate oxide scaling limit is around 2 nm. Moreover, large gate leakage current due to direct tunneling causes serious performance degradation and intolerable power consumption. Additionally, fabrication of thin-film capacitors using higher dielectric constant materials can provide higher charge storage densities, and enable capacitor fabrication using planar technology for the requirements of dynamic random-access memory (DRAM). Metal oxides, such as zirconium oxide (ZrO₂), hafnium oxide (HfO₂), and tantalum oxide (Ta₂O₅), are potential candidates for these purposes. However, most of the high-k films suffer from a high leakage current after being processed at a high temperature.

ZrTiO₄ with 20 mol % Zr replaced by Sn ions has proved to be one of the most popular high dielectric materials for microwave devices. Recent work has examined the feasibility of applying ZST thin films to memory and gate dielectric applications. Most ZrTiO₄-based thin films prepared by pulse laser ablation or rf sputtering with high physical power in the deposition process induces the formation of the interface layer and high-surface roughness. The sol-gel process and chemical vapor deposition (CVD) are chemical routes to fabricate the nanopowders and thin films. The sol-gel process can coat larger surfaces even with an odd geometry without using expensive vacuum systems as the CVD process does. Generally, the control of the process parameters is critical in making a good homogeneity and crack-free film. Sol-gel derived (Zr₅Sn₅Ti₄O₂₆) (ZST) thin films have been prepared. However, the relationship between the microstructure and the electrical properties was not carefully reported. Leakage current is an issue of critical concern in memory device applications. Many of these dielectric thin films exhibit significant thickness-dependence on structure and electrical characteristics. In this study, a modified sol-gel process was used to obtain thinner ZST films. We focused on the effects of film thickness on the microstructure and electrical properties of the ZST films.

High-purity zirconium oxychloride (ZrOCl₂ · 8H₂O), stannic chloride (SnCl₄ · 5H₂O), and tetrabutyl titanate [Ti(OC₄H₉)₄] were used as starting materials. Methanol was used as the solvent for the precursors for controlling viscosity and cracking of the thin film. Metal ratios in the precursor mixtures were Zr:Sn:Ti (in molar ratio) = 4:1:5. The precursor solution was mixed and refluxed at 68°C for 3 h. Unlike the prior work, without aging, the solution was centrifuged for 20 min and the top part of the clear solution was pipetted out for the coating to obtain the thinner film, compared to the conventional sol-gel process. The concentration of the final solution was adjusted to approximately 0.25 M. A sample of p-type Si(100) was cut into 2 × 2 cm² squares and washed carefully according to standard RCA methods. About 50 μL of the solution was spin-coated directly on the Si(100) substrate at 3000 rpm for 15 s and then 4200 rpm for 15 s to form a uniform wet film at room temperature. After each spin coating, the sample was heat-treated at 250°C according to the differential thermal analysis (DTA) (not shown) in air atmosphere on a hot plate to burn out the solvent and solidify the film for 3 min. This step was repeated several times to achieve the desired thickness of the film. Then the films were finally annealed in air at 700°C for a total of 30 min at a ramp rate of 2°C/min to crystallize the amorphous films. The ZST film thickness as a function of the numbers of the coating cycle is tabulated in Table I. The thickness was measured and averaged from a series of SEM photographs taken at the cross section of samples. The averaged film thicknesses treated at 250°C and finally annealed at 700°C were 26, 78, and 134 nm for 1, 3, and 5 coating cycles, respectively. The films were characterized by a rotating X-ray diffraction (XRD), a X-ray photoelectron spectroscopy (XPS), a high resolution transmission electron microscopy (HRTEM), and a conductive atomic force microscope (AFM).

The leakage current densities of the ZST films were electrically characterized via computer-controlled HP 4156 by dc to 40 V. Figure 1 shows a typical XPS analysis of the 78 nm ZST thin film, indicating the compositions of the film are Zr–Sn–Ti–O, and no chloride is detected. The ratio of the oxygen to metals (Zr + Sn + Ti) measured by XPS was around two in all samples. The composition of films with different thicknesses shows the similar results. A stable ZrTiO₄ orthorhombic phase may tolerate the variation of Zr/Ti mole ratio from 0.72 to 1.22. The mole ratio of Zr/Ti identified by XPS was approximately 1.05 which satisfied the requirement of the stable phase.

The film thickness strongly influences the structure of the crystalline phase in the high-temperature annealed film. Figure 2 shows XRD patterns of sol-gel derived ZST thin films with different thicknesses. The thicker ZST film annealed at 700°C contains a crystal-line phase corresponding to orthorhombic ZST with (111), (110), and (002) orientations which are well consistent with the ZST pat-
tern found in JCPDF file no. 81-2214. The 26 nm ZST film has a pronounced preferred orientation. However, it is crystalline if the thickness is 100 nm. The crystallization process includes two mechanisms, nucleation and grain growth. With the shrinking of the film thickness, the surface energy, which favors the suppression of the grain growth, plays a dominant role. Therefore, under the same annealing condition, the 26 nm film is more difficult to crystallize than the 78 nm film. In addition, the crystal structure of the film is strongly dependent on its thickness. The 26 nm ZST shows an orthorhombic phase with (111) orientation, while the 134 nm film shows an orthorhombic phase with multiorientation. The strongest peak is (111), which can be explained on the basis of Wulff’s theorem since the relative values of ZST thin-film surface energy defined as the surface energy of the [hkl] surface energy of (111) $\times 100$, calculated by Nakagawara et al. for [111] and [110] planes are 100 and 120, respectively. The noise level is high and the only visible peak is seen as in (111) for film thickness less than 78 nm. In the XRD spectra, the signal for (111) is only four times the noise of the background for film thickness below 78 nm, and the minor peaks, if they exist, are indistinguishable from the background. To clear up this ambiguity, more than four separate experiments were done for each thin film sample. The signals of XRD peaks of the experiments are attached together, and were plotted in one chart. Still only the (111) peak is noticeable for film thicknesses below 78 nm. A XRD experiment with longer scan time was also pursued and same result appeared. Therefore, the suggestion is drawn that 26 nm film with preferable direction was obtained. The XRD results show that no other secondary phase is present in the film in Fig. 2, probably due to the sensitivity limit of the instrument or the small volume ratio of the crystal. Further studies using TEM or SIMS are needed to clear up this issue.

The film thickness can further influence the crystal size in the ZST film. With the film thickness increasing, the films show more intense diffraction peaks (Fig. 2b), indicating a greater volume percentage of the crystalline phases. The insert in Fig. 2 shows the correlation between the crystal size ($D_v$) and the film thickness. According to the XRD line broadening by using Scherrer formula, the averaged crystal size for films annealed at 700°C are 10, 23, and 23 nm for 26, 78, and 134 nm films, respectively, indicating the crystal size of polycrystalline ZST films were not increasing with the increase of film thickness and all crystal sizes were smaller than the film thickness and independent of film thickness.

The typical morphology for 700°C annealed ZST film of thickness 26 nm was examined by AFM, as shown in Fig. 3. The roughness of root mean square (rms) of all deposited films was less than 0.9 nm, indicating that smooth ZST films can be deposited on a p-type Si(100) substrate using the proposal sol-gel technique. Figure 4 shows a cross-sectional SEM image of a 134 nm ZST film annealed at 700°C. The image demonstrates a smooth coating surface on the ZST thin film, also indicating that the film has good

| Table I. Film thicknesses as function of numbers of coating cycles. |
|------------------------|-----------------|
| Number of layers | Thickness (nm) |
| 1 | 26 ± 6 |
| 3 | 78 ± 1 |
| 5 | 134 ± 8 |

Figure 1. XPS analysis of the ZST thin film with 78 nm.

Figure 2. (a) XRD patterns and (b) fwhm and highest intensity of sol-gel derived ZST thin films with different thicknesses annealed at 700°C for 30 min.

Figure 3. AFM image of ZST film with thickness of 26 nm.
deposition quality, ZST grains with sizes ranging between 15–30 nm were observed in this cross section, which are very close to the crystal sizes calculated in Fig. 2. Additionally, HRTEM analysis shows that about a 4–5 nm interface layer with amorphous phase appears independent of the thickness.

Figure 5 shows the leakage current density of ZST films as a function of bias voltage and applied electric field. The leakage current densities of polycrystalline ZST film are in the order of $3 \times 10^{-9}$ A/cm² and $1.7 \times 10^{-7}$ A/cm² at an applied field of 3 MV/cm for film of thicknesses 34 and 78 nm, respectively. The leakage current of preferred orientation ZST film is in the order of $2 \times 10^{-6}$ A/cm² at an applied field of 3 MV/cm. Results of this study demonstrate that the leakage current of preferred orientation ZST is lower than that of polycrystalline ZST, since the high-temperature annealed film forms a polycrystalline phase, which greatly contributes to the high leakage current. Since about a 4–5 nm interface layer with amorphous phase appears independent of the thickness, the reduced leakage current is more likely to be due to a greater proportion of an amorphous phase present in 26 nm ZST film. Furthermore, referring to the inset of Fig. 2b, the crystal size for film of thickness 26 nm is smaller than films of thickness 78 and 134 nm. Because of the presence of more grain boundaries across film with smaller crystal size which would delay the current conduction from one electrode to the other, the lower leakage current density exhibits in 26 nm film. However, the current density is small enough compared to the conventional silicon oxide with the same thickness and well satisfies the target range for the DRAM applications (1–5 $\times 10^{-7}$ A/cm²). The prepared ZST films exhibit dielectric constants of 15-23. Mays et al. suggested the composition of the CVD-prepared ZST films influences the dielectric constants. However, the composition of our sol-gel derived films with different thicknesses shows similar results. The lower dielectric constants as compared to those of films deposited by pulsed laser ablation (38) may be due to the formation of an interface layer between ZST film and the Si substrate but the value is similar to those of CVD film (20-30) and sputtered films (11-18). More detailed studies will be made.

In summary, smooth ZST thin films can be deposited on a p-type Si(100) substrate using a sol-gel technique. A ZST film of thickness 26 nm demonstrated a preferred orientation, while films of thickness 75 nm or more illustrate a polycrystalline structure. The crystallite size of ZST films for films of thickness 26, 78, and 134 nm are 10, 23, and 23 nm, respectively. Leakage current densities in polycrystalline films are higher than those in the preferred orientation film. The order of leakage current density is less than $10^{-7}$ A/cm at 3 MV/cm from all films, indicating that ZST films with high quality and low leakage current can be obtained by the presented sol-gel process.

Acknowledgments

The authors acknowledge S.S. Wang of Fooyin University for preparing the samples and the Advanced Optoelectronic Technology Center, National Cheng Kung University, Taiwan, for support through equipment and cooperation.

National Nano Device Laboratories assisted in meeting the publication costs of this article.

References