Effects of anodisation parameters on thin film properties: a review


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Effects of anodisation parameters on thin film properties: a review

Y. H. Wong∗1, M. G. Affendy1,2, S. K. Lau1, P. C. Teh1, H. J. Lee3, C. Y. Tan1 and S. Ramesh1

Electrochemical anodisation is a well-received method in the complementary metal-oxide-semiconductor field as it is advantageous; best performed at room temperature which translates into being more affordable and a simple alternative to form nano-structured oxide films for different metals. The quintessential parameters involved allow numerous formations of metal oxide films according to desired morphology and thickness. Therefore, this paper aims to review the effects of anodising parameters such as applied voltage, concentration, temperature, time, current density and post-anodisation annealing among them.

Keywords: Anodisation, Thin films, Applied voltage, Temperature, Thickness

Introduction

For the past few decades, complementary metal-oxide-semiconductor (CMOS) has received huge attention due to their potential use in advanced areas of sensors, photovoltaic cells, biomedical and photocatalytic engineering.1-3 In addition to that, these metal oxides of controlled micro/nano-morphologies have found significant applications such as nanomaterial synthesis, super capacitors, water purification systems, and self-cleaning and self-sterilising materials.4-6

Generally, the application performance of metal oxides is determined by their structure and surface features.7 Thin oxide films are widely favoured compared to bulk materials because of cost considerations, processing flexibility, and suitability for various substrates, types and shapes. Since SiO2 has been well explored in past literatures, several oxides with higher dielectric constant have been proposed as alternatives to it. Among them are ZrO2, TiO2, Al2O3, CeO2 and HfO2 to name a few. Taking ZrO2 as an example, it is deemed to be one of the highest potential candidates due to its wide band gap, high conductivity barrier and high dielectric constant.13

There are different methods, both chemically and physically, which are available to prepare these metal oxides on Si substrate for instance chemical vapour deposition (CVD),14 spray pyrolysis,15,16 sol-gel,17 thermal oxidation,18-20 and reactive sputtering.21 However, these methods require high thermal budget and huge amount of time. In addition to that, these properties may result in a damaging effect on further sub-micrometer fabrication process.22 Thus, it is crucial then to search for and implement a method which is relatively low in thermal budget as well as consuming less time.

With that taken into account, electrochemical anodisation of metals can be widely considered as the suitable method to allow the formation of metal oxide films. By definition, anodisation is a simple process of converting metal into its oxide in a liquid bath under applied voltage or current. Anodisation is preferred as this particular process can be performed at room temperature; thus, it offers a cheaper and easier alternative for producing nano-structured metal oxide films on a range of metals and alloys.23 As a result, the morphology and the thickness of metal oxide formed depend on the parameter applied. According to Lewandowska,24 anodic oxidation of alloy in an acidic electrolyte is deemed beneficial in the biomedical field as this method may produce an effective barrier between alloy and the surrounding environment without affecting the bio-compatibility of the material.

Apart from the importance for a practical application in industry, clarification of the factors controlling the dielectric properties of anodic oxide film has essential significance for an understanding of the fundamental anodisation mechanism.25 It is therefore vital for researchers to investigate the effects of anodising conditions which include applied voltage, current density, concentration, temperature and type of electrolyte. For example, the type of electrolyte used and electric conditions applied can affect the surface morphology, chemical composition and crystalline structure of the oxide films formed.26,27 Furthermore, geometrical features of the nanopores, like the pore diameter, interpore distance, thickness of the porous oxide layer etc. are in a strong relation with anodising conditions as mentioned earlier.28-30

Thick and porous oxide films can be fabricated via a high voltage to facilitate dielectric breakdown. These films increase the surface roughness of titanium and provide high bond strength between the oxide film and the titanium substrate. Moreover, the hardness of titanium

1Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia
2School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham, West Midlands, B15 2TT, United Kingdom
3Center for Photonic Technologies, Universiti Tenaga Nasional, Bandar Baru Bangi, Selangor 43650, Malaysia
*Corresponding author, email yhwong@um.edu.my

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substrate metal close to the oxide layer could be improved by anodic oxidation due to incorporation of oxygen into titanium metal.31

Kuromoto et al.32 has stated that the colouration of TiO2 oxide produced through anodisation can be indicative to the thickness of the oxide film. Furthermore, this relation between colour and thickness of oxide film depends strongly on the process and the nature of the electrolyte.33 Any change in these parameters can modify the colouration of the oxide surface. Sul et al.33 have indicated that the electrochemical growth behaviour of the oxide film is strongly dependent on anodic parameters such as electrolyte concentration, applied current density, anodic forming voltage, the given temperature, agitation speed and the surface area ratios of cathode to anode.

Therefore, with all of the parameters mentioned above, it has become an imperative issue on what are the optimum conditions for preparing the anodic metal oxide films in order to provide the best properties. Important and frequently applied parameters which are applied voltage, temperature, time and post-anodisation annealing will be discussed from past literatures to determine their impacts on the properties of produced metal oxide film.

Anodisation of thin film and growth modes

Anodisation is a relatively simple and easy method to form a gate dielectric. Yet, only limited effort has been done so far to investigate properties of anodised ZrO2 thin film. One of the reasons is because this technique is not a single flow process. High purity of metal thin film is first deposited with the assistance of physical vapour deposition (PVD) technique, such as sputtering followed by anodisation to grow the metal oxide dielectric.

Anodisation is a highly versatile technique as it can be conducted under room temperature. In addition, the apparatus setup is comparatively easier and cheaper than other advanced thin film deposition technologies.22 Prior to the execution of anodisation process, some preparation on the sputtered Si has to be done. First, Zr deposited Si has to be attached to the conductive metal (commonly Cu or Al) using silver paste. The conductive metal has then to be connected to the positive potential of electrochemical cell, where the negative bias has to be connected to platinum electrode as illustrated in Fig. 1.34 Acidic solution such as hydrochloric acid (HCl), nitric acid (HNO3) and sulphuric acid (H2SO4) or alkaline solution such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) can be used as electrolyte. However, alkaline solution is better fit for anodisation process in comparison to acidic solution. This is because large quantity of hydroxide is produced in the alkaline solution and it serves as the source of oxygen to grow the oxide gate layer.35–37 This is sometimes known as wet oxidation process. On the other hand, if the dielectric layer is grown by direct heating inside a furnace in an oxidation-contained ambient, it is then called the dry oxidation process.

The growth rate of oxide in wet oxidation is much faster than dry oxidation because oxygen molecules are bulkier than hydroxide ions so they take longer time to diffuse. The rapid growth rate of ZrO2 is undesired as sometimes it may degrade the quality of thin film; this is because it might be difficult to control the oxide formation mechanism as well as inducing contamination.

This rapid growth of oxide through anodisation process is well compensated by the unique crystal structure formation under room temperature as compared to other synthesis techniques. In general, ZrO2 can exist in three different structures with respect to the processing and post treatment temperature.38 Via anodisation method, it is able to generate high thermal stability phase at low temperature. This is an achievement offered by anodisation as compared to other deposition techniques. Formation of different crystal structures correspond to various voltages applied was reported by Lockman et al.22 Only native amorphous ZrO2 was produced when there was no voltage supplied to the electrochemical cell. Then high temperature phase of cubic or tetragonal ZrO2 was formed at low anodisation voltage of 5 V. By subsequent addition of anodisation voltage, monoclinic phase of ZrO2 (m-ZrO2) was found present in the thin film. After that, grain size continues to grow with anodisation voltage and at the same time crack was identified on the thin film. The crack phenomenon was observed at about 25 V of voltage supply. Such defect is highly undesirable as it significantly affects the performance of electrical properties especially the dielectric constant. It was suggested that the amount of defects can be controlled by varying the anodisation voltage and the purity of anodised ZrO2 thin film can be maintained owing to low diffusivity of impurities in the thin film.

There are three possible growth modes during the deposition process namely Frank-van der Merwe, Volmer-Weber and Stranski-Krastanov as illustrated in Fig. 2a–c, respectively.39 Basically, there is no restriction in the growth mode for every deposition process. The growth mode is highly dependent on the deposition temperature and surface energy of film and substrate.

In the Frank-van der Merwe growth mode, adatoms form a complete monolayer on the surface of substrate followed by a second layer. This is because adatoms are able to bond intensively with substrate. This layer-by-layer growth usually results in a single crystalline structure.40 Volmer-Weber is another growing mechanism in which adatoms are prone to attach to each other rather than to the substrate. Therefore, the adatoms form a
Effects of applied voltage on thin film morphology

Basically, the metal oxide films produced from electrochemical anodisation attain distinct morphology and phases present which were characterised thoroughly. In that matter, both issues can be investigated with respect to the applied voltage in order to understand the effects of voltage in the mechanism of growth of oxide film during anodisation.

First, morphology evaluation of oxide films is normally performed by scanning electron microscope (SEM). According to Kuromoto et al., TiO₂ films were produced on Ti samples by anodic oxidation at different voltages. Figure 3 shows two types of surface morphologies; a non-porous structure on natural Ti [Fig. 3a] and a porous structure where the pore size increases with increasing applied voltage [Fig. 3b–f].

From the AFM evaluation, the pores began to develop and become more uniform with increasing applied voltage. The process occurred with the oxide film breaking down locally attributed by the dielectric breakdown. As a result, the porosity and pore size increased. This morphology resembled the results obtained by Kawashita et al. on the surface of Ti anodically oxidised at 180 V in 2 M H₃PO₄ electrolyte. Larger pore size observed is due to the interconnections of some pores with each other.

Moreover, the uniformity of oxide film can be observed as well in the works of Xing et al. At low potential (200 mV), the film surface is relatively flat, with only a few grains can be seen. However, with increasing potential values, multiple individual grains of with an average diameter of approximately 100 nm emerged on sample surface. Lastly, at the highest potential (2000 mV), grain shapes appeared to be clearer, and uniform throughout the film surface. According to past literatures, these nanoscale grains formed on Ti anodised film surfaces are anatase nanocrystals. Thus, it is deemed advantageous for the production of crystalline Ti oxides by implementing high applied voltages.

Besides that, Fig. 4 depicts the FESEM images of the ZrO₂ thin film surface after anodisation process in 1 M NaOH for 15 min at a 10 V, b 20 V, c 30 V, d 40 V and e 60 V. Similar to previous observations, the surface of the film anodised at low voltages such as at 10 V [Fig. 4a] and 20 V [Fig. 4b] are relatively smooth. The grains appeared spherical in shape with diameters measured in the nanoscale. The grains are spherical with diameters in the nanoscale. Following a parallel pattern, the diameter of the grains increased when anodisation voltages were increased. At 40 V, blistering and cracks are very obvious on the sample’s surface. Anodisation at even higher voltage of 60 V leads to more blistering and severe delamination of the oxide from the substrate [Fig. 4c].

Effects of applied voltage on thin film formation mechanisms

Normally, film formation via anodic oxidation begins with the following steps; first, the natural TiO₂ particles grow, coalesce together and form a smooth region. After a while, some areas begin to develop cracks and become porous. As the applied voltage increases, the film breaks down locally, hence regions of original and altered film develop simultaneously. The resulting film is a combination of flat and porous regions.

When the anodic voltage is at a high value, TiO₂ film formation occurs as a result of the migration of O⁻ ions into the metal/film interface and migration of the Ti⁴⁺ ions from metallic Ti to the film/electrolyte interface. There are many reactions occurring during the process and the most relevant reactions that participate in the film growth are those that give rise to O₂ and TiO₂. The O₂ formation in the film can create a pressure that can destroy the film. Dielectric breakdown was detected when voltage is increased. High electric field between the inner and outer interfaces of the film cause it to break down and give rise to pore formation. At this stage, the TiO₂ growth rate becomes smaller than during the initial stage. The pores in the surface
of the film are filled with the electrolyte favouring the passage of the current.

In the case of ZrO$_2$, it is accepted that the inward migration of the O$^{2-}$ is the controlling process for the oxide growth. In the case of ZrO$_2$, it is accepted that the inward migration of the O$^{2-}$ is the controlling process for the oxide growth.46 O$^{2-}$ is produced by water dissociation.47 Figure 5 is a model explaining the growth of ZrO$_2$ as a function of anodisation voltages. This proposed mechanism is adapted from those established by Azuma et al.,48 Abdel Rahim et al.,49 and Mamun et al.50 for anodised Zr foils.

Assuming that the anodisation of thin Zr film follows the same route as the Zr foils, therefore, once the initial oxide layer formed, which is normally amorphous as depicted in Fig. 5a, a growth can be possible when O$^{2-}$ is moving inwards through this initial layer to the metal/oxide interface. If O$^{2-}$ is not transported inwards, the growth would stop and the underlying metal layer maybe protected. The Zr metal layer is shown as the darker shaded region in the figure.

As shown in Fig. 5b, anodisation at 5 V may lead to the formation of crystalline ZrO$_2$ nanocrystals, represented by shaded circles, embedded in and amorphous or non-stoichiometric ZrO$_2$ matrix. The size of the crystallite is in the nanoscale and this contributes to the broadness of the X-ray diffraction (XRD) peaks (Fig. 6). If there is a concentration gradient of O$^{2-}$ across the film with less O$^{2-}$ near the metal/oxide interface then higher concentration of oxygen vacancies is expected in this region. Consequently, this would promote the nucleation and stabilisation of tetragonal or cubic ZrO$_2$.

With an increase of the anodisation voltage to 10 V, more O$^{2-}$ ions are transported across the oxide layer [Fig. 5c]. When more O$^{2-}$ enters the oxide, nanocrystals will grow presumably by the migrations of both cations and anions to the boundary wall of each crystal increasing its size. The shaper and more intense XRD peaks reflect the increase of the crystallite size of the tetragonal or cubic ZrO$_2$. While the inner layer near the substrate is crystalline with either tetragonal or cubic ZrO$_2$, the outer layer of the oxide is predominantly amorphous. Regardless of its crystallinity, as a whole, the oxide is demonstrating an insulating property with the preferred
orientated ZrO₂, acting as a leakage path when a transverse voltage is applied.

As the anodisation voltage is increased to 20 V, monoclinic ZrO₂ can start to be detected by the XRD. The peaks of tetragonal or cubic phases still retain but the intensity is slightly reduced. Two possibilities can be concluded: (1) the transformation of high temperature phase to monoclinic phase or (2) transformation of the amorphous oxide to monoclinic ZrO₂. At a high enough voltage, according to Mamun et al., oxygen evolution is possible on the hydrated oxide. This occurs by the removal of water from the amorphous film and crystallisation starts. Since there is excess oxygen in the region, monoclinic ZrO₂ is thought to nucleate and grow at the surface of the film.

Growth of oxide at 20 V is shown schematically in Fig. 5d. As the oxide is consisted of ZrO₂, with different phases and orientations the insulating property of the oxide is much enhanced, in which current passing through the oxide is minimised when a transverse voltage is applied.

Often, crystallisation of the outer layer is followed by the formation of cracks within the film. Cracks lead to the physical breakdown on the film as seen for the sample anodised greater than 30 V where obvious blistering has occurred. This can be illustrated in Fig. 5e for sample anodised at 30 V. At even higher voltages, oxide delaminates from the substrate; with the degree of delamination more severe as the anodisation voltages are increased to 60 V.

In Fig. 5f, oxide delamination is shown. As the films have cracks, oxygen penetrates through the layer via these cracks towards the oxide/substrate interface. As this region is consisted of tetragonal or cubic ZrO₂, with the excess amount of oxygen existing in the vicinity of the crystals, transformation to monoclinic will occur in this region. In addition to that, the transformation would lead to volume changes within the oxide, inducing oxide to crack. Oxygen penetrates through the oxide layer inwards via the cracks may also oxidised the underlying Si.

Effects of temperature on thin film

In the works of Lin et al., on the effects of annealing temperature on the photocatalytic activity of TiO₂ thin films, the surface morphology was examined as shown in Fig. 7. The surface roughness appeared to increase with annealing temperature although AFM results have stated that little growth was evident on TiO₂ grain sizes.
This can be attributed to minimal densification with the grains becoming more faceted with the increase in annealing temperature. It is worth noting that the film thickness remained the same at ∼255 nm for all TiO2 films at different annealing temperatures.

Temperature also affects the anodising behaviour of thin films, as investigated by Ono et al. of anodic oxide films formed on niobium. From the voltage–time curves presented, the slopes, dV/dt derived from them can be seen in Fig. 8. As the temperature increases, the thickness of the film increases too with consideration that the film property is similar and the oxide dissolution during film growth is perceived negligible. Increase in electricity consumption was the factor for thickness issue.

**Effects of time on thin film**

Jeon and Hwang studied on the effect of anodising time towards the electrical characteristics of zirconium oxide by anodisation employing ammonium tartrate electrolyte (pH = 6.7) as the electrolyte. It is found that the surface roughness is dependent to the anodising time, in which increasing the anodising time will improves the surface smoothness. Also, as anodising time increases, thickness of anodic oxide ZrO2 films will also increase. However, the thickness increases slowly at longer anodising time, as the saturated oxide thin films are achieved. This shows that anodisation is a self-limiting growth process, offering a better control over the oxide thickness.
electrical characteristics at 400 s are proposed to be the most acceptable anodising time, with relatively low leakage currents of $1.5 \times 10^{-3}$ A cm$^{-2}$ at -1 V, high breakdown voltage of 27 MV cm$^{-1}$, acceptable effective oxide thickness (EOT) of 11.5, and comparable interface state density of $(5.5-6.5) \times 10^{11}$ cm$^{-2}$ eV$^{-1}$. The ZrO$_2$ produced by anodisation at 400 s are calculated to have the high k value of 13.9. At the anodising time lower than 400 s, it was found to be in the under-anodised condition, in which Zr metal layer are present in the interface of ZrO$_2$/Si. The leakage current is also found to be relatively high with anomalous high capacitance. In other hands, at longer anodising time of 1200 s, it was found to have relatively low amount of fixed charge density, which then can induced the lower mobility characteristics of the device. Therefore, it is important in obtaining the optimising time of anodisation in order to have the most optimum features for MOS technology.

Allah et al. have studied on the kinetic of anodic oxide films on Zr electrode in 1 M NaOH. The oxide build are observed for the first 30 min, longer than anodisation time of 30 min, dissolution takes place. The rate of dissolution on the other hands also depends on the defects that presents in the oxide films.

**Effect of post-anodisation annealing on thin film**

Post-anodisation annealing is conducted to reduce the damage during the processing steps after the formation of gate dielectric. This step is a way to improve mechanical and electrical properties of dielectric thin film through modification of crystallography structure and grain morphologies. In other words, post-anodisation annealing is indispensable to acquire high quality and good performance of gate dielectric. In addition, the effects of post treatment are often manifesting for ZrO$_2$.

**Relationship of annealing temperature and crystal structure**

Typically, ZrO$_2$ is a polymorph which exists in three different (monoclinic, tetragonal and cubic) structures correspond to the surrounding temperature. Orthorhombic structure is another possible state of ZrO$_2$ which normally occurs at relative high pressure as compared to the other three polymorphs. Figure 9 is a phase diagram of ZrO$_2$ which explains the transformation of these crystallography structures.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Dielectric constant</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoclinic</td>
<td>19.7</td>
<td>5.42</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>46.6</td>
<td>6.40</td>
</tr>
<tr>
<td>Cubic</td>
<td>36.8</td>
<td>5.55</td>
</tr>
</tbody>
</table>

Combination of PVD and anodisation can possibly generate tetragonal and cubic structures at low temperature. On the contrary, monoclinic phase is the predominant structure that existed in the as-deposited ZrO$_2$ with reactive sputtering, atomic layer deposition (ALD) and metal-organic CVD (MOCVD). Among the three crystallography cVds mentioned, t-ZrO$_2$ would be the most suitable candidate to act as gate oxide due to its good dielectric and insulating properties. The theoretical values of dielectric constant and band gap energy of monoclinic, tetragonal and cubic structures are given in Table 1 and Fig. 10.

Unfortunately, fabrication of solely t-ZrO$_2$ is impractical due to temperature stability. Therefore, a mixture of these three phases is often observed for all deposition techniques. This explains the fact where $\kappa$ of ZrO$_2$ usually falls around 25. The only exception is that anodisation can produce large quantity of tetragonal structure; further annealing is required to yield a reasonable amount of monoclinic structure to stabilise the metastable tetragonal phase. Annealing is carried out for reactive sputtering, ALD and MOCVD to produce tetragonal phase in the predominant monoclinic structure and hence oppose to the course of anodisation. Aside from that, annealing temperature that is applied in anodisation is much lower than the other methods because monoclinic phase is able to crystallise at relative low temperature as compared...
to the tetragonal and cubic structures. In brief, the phase transformation is tabulated in Fig. 11.

The ultimate goal of current ongoing research is to determine the optimum mechanical and electrical properties that can be achieved by ZrO₂ through the alternation in crystal structure. Currently, the best conformation of ZrO₂ gate dielectric is to compose both monoclinic and tetragonal structures in thin film. Sometimes, cubic phase is incorporated into the thin film to acquire high thermal stability.

**Relationship of annealing temperature and grain morphologies**

The effect of annealing on the ZrO₂ grain morphologies is similar to the basic zone model as proposed by Movchan.
and Demchishin,\textsuperscript{61} namely MD diagram. The MD diagram is suggested primarily for temperature used during deposition, it may also be used for the grain growth mechanism during normal annealing process.

The effect of annealing temperature on grain morphologies is rather straightforward. For instance, the void density is drastically reduced at high annealing temperature because atoms have high mobility in restructuring themselves into a more closed pack structure which is accompanied by the grain growth. As a result, this reduces the accumulation of residue stress in the system therefore improves the performance of gate dielectric. On the contrary, high mobility of atoms creates a rough surface and it is undesirable for the precision of CMOS fabrication. Thus, there is a limitation for the annealing temperature therefore the optimum temperature is still under investigation.\textsuperscript{62}

XRD analysis on the annealed zirconia dielectric

Chinchanalatpure \textit{et al.}\textsuperscript{63} studied the effect of post-annealing on ZrO\textsubscript{2} thin film where suspension of ZrO\textsubscript{2} is first synthesised via the sol-gel method followed by spin coating on Si surface. Afterwards, two of the ZrO\textsubscript{2} deposited substrates are calcinated at 400 and 700°C for 2 h. Sol-gel technique is suggested because of its high compatibility in the generation of ceramic and dielectric film in the micrometer thickness range.

\textbf{Figure 12} shows XRD result where only t-ZrO\textsubscript{2} is observed when it is annealed at 400°C. Then, monoclinic phase started to crystallise and appear at 700°C of calcination temperature. This is because tetragonal phase of ZrO\textsubscript{2} is stable at 1205–2377°C. Hence, if sufficient heat energy is supplied to ZrO\textsubscript{2} at temperature below 1205°C, recrystallisation of ZrO\textsubscript{2} will take place to yield the monoclinic phase. However, information regarding transformation of crystallography structure is limited as only two calcination temperatures were involved in this project. More parameters should have been tested to provide a better overview on the change in phase. The tetragonal
diffraction peaks are identified at 29.50° and 33.15° while monoclinic diffraction peaks are found at 28° and 51°.

**Capacitance–voltage (C–V) characteristic of the annealed zirconia thin film**

Chinchamalatpure *et al.* discussed on the relationship between capacitance and voltage behaviour of annealed ZrO₂. Figure 13 shows that the flat band voltage of p-type silicon substrate happened at ~0.5 V. The capacitance of ZrO₂ dielectric layer decreases drastically when negative bias is applied to the gate voltage. This phenomenon is due to accumulation of charge carriers on the MOSFET structure. However, when gate voltage exceeded ~0.5 V, the capacitance is reduced and this gradient reduction portion is commonly identified as the depletion region. Lastly, the curve becomes relatively flat with no further reduction for capacitance above 0.5 V.

Obviously, the capability of ZrO₂ dielectric to store charge increased tremendously if annealing is conducted during fabrication. The charge accumulation of as-ZrO₂ is about 225 F. Capacitances of ZrO₂ calcinated at 400 and 700°C are roughly 410 F and 820 F. The increment in capacitance happens because of the co-existence of monoclinic and tetragonal phases which act as a good diffusion barrier towards charge carriers. On top of that, integration of ZrO₂ and Si at the contact interface is improved which in turn enhanced the capacitance property.

**Current–voltage (I–V) characteristic of annealed zirconia thin film**

Another interesting result reported by Chinchamalatpure *et al.* is the current to voltage properties of ZrO₂ dielectric which measured the leakage current of thin film when electric field present in the thin film. The bias applies at the gate contact is highly dependent on type of substrates. For instance, positive potential is used as a p-type substrate to prevent flow of electrons from source to drain which will then possibly affect the intended current measurement. Besides, good insulation is a result of low leakage current across the thin film. The I–V characteristic of the ZrO₂ is indicated in Fig. 14.

Saturation leakage current of ZrO₂ thin film is low with respect to annealing process at high temperature. The average saturation leakage current density of as-deposited ZrO₂ thin film is about 10 A cm⁻², whereas (400–700°C) annealed ZrO₂ has leakage current density of 10⁻¹ and 10⁻² A cm⁻², respectively. The leakage density is reduced at the order of 10 for these three samples. One explanation is that thickness of film continues to grow at higher annealing temperature which will further impede the charge flow. At high temperature, defects found on the interface are eliminated hence allow formation of smooth ZrO₂ at the interface. This is significant as defects are always served as the transportation path for charge carriers such as electrons and holes.

**Effect of annealing condition on the EOT of zirconia**

The environment in which the annealing process is carried out has a big impact on the thickness of ZrO₂. This relationship is defined by Yao and Tay. First, a layer of ZrO₂ is deposited on Si substrate through CVD at 500°C. After that, rapid thermal annealing (RTP) is conducted to the samples at three types of modes: 800°C for 60 s, 800°C for 2 s and 1000°C for 2 s. The rapid annealing for 2 s is referred as spike condition. Five different annealing environments are involved which include nitrogen gas, dry hydrogen, wet hydrogen (15% of water), dry oxygen and wet oxygen (15% of water) as shown in Fig. 15. ZrO₂ is found to be thicker if it is annealed under ambient environment with abundant oxygen molecules. In addition, it is also clear that nitrogen gas provides the slowest growth rate for ZrO₂ thin film as compared to the other four conditions. This phenomenon is because Zr and ZrO₂ has a poor diffusion barrier towards oxygen. As a result, oxygen can readily diffuse into the atomic structure and oxidise Zr into dielectric film. On the other hand, thickness of ZrO₂ dielectric continues to grow when longer annealing time is allowed. As an example, thicknesses of ZrO₂ annealed at 800°C under ambient environment are recorded to be 18.1 and 31.4 Å for 2 and 60 s, respectively.

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**Figure 13** C–V characteristic of annealed zirconia thin film (retrieved from Chinchamalatpure *et al.*).

**Figure 14** I–V characteristic of annealed ZrO₂ thin film (retrieved from Chinchamalatpure *et al.*).
Leakage current as a function of EOT

Research by Yao et al. provides a good explanation on the leakage current of ZrO₂ with respect to EOT. Samples annealed at various RTP conditions undergone the current test by applying −1.0 V to the gate voltage. Figure 16 illustrates the leakage current density is decreased as the EOT of ZrO₂ is increased. For example, the leakage current densities of 18.1, 31.4 and 32.0 Å ZrO₂ grew on ambient environment are about $8 \times 10^{-6}$ A cm$^{-2}$, $3 \times 10^{-8}$ A cm$^{-2}$ and $7 \times 10^{-9}$ A cm$^{-2}$, respectively. This implies that ZrO₂ is a good insulator against electric current, since the leakage current density with magnitude lower than $10^{-5}$ A cm$^{-2}$ is able to achieve for −0.1 V of gate potential applied. Furthermore, the leakage current curve of SiO₂ generated under dry oxygen source is plotted in the same graph to ease the comparison. For 18.1 Å, the leakage current of ZrO₂ is about $10^{-7}$ A cm$^{-2}$, whereas SiO₂ records 1 A cm$^{-2}$ with the similar thickness. As a result, it is clear that the capability to hinder leakage current is enhanced by replacing SiO₂ with ZrO₂. The leakage current of ZrO₂ produced in nitrogen gas is also higher as compared to oxygen because of the thin dielectric film.

Surface morphologies of annealed zirconia thin film

The surface morphologies of ZrO₂ thin film are inspected by Khojier et al. Zr thin film were deposited on a glass substrate via direct current magnetron sputtering method followed by the annealing in tube furnace at temperature 100–500°C. Aside from that, atomic force microscopy (AFM) is the characterisation instrument used to study the surface morphologies such as surface roughness and grain size of samples. Figure 17 presents the AFM result. It is observed that the surface of ZrO₂ annealed at high temperature is rough. In addition, granular structure is also formed in ZrO₂ thin film and the grain size increases with the annealing temperature. Rough surface and bigger grain size of ZrO₂ thin film are attributed to high mobility of atoms at high annealing temperature where ZrO₂ atoms have sufficient kinetic energy to transport to the nearby grain and then coalescence into a bigger size grain. Non-uniform surface with deep valleys are highly undesirable as this creates a variation in the applied voltage and increases the threshold voltage.

Conclusion and future challenges

Clarification of factors regarding the electrochemical anodisation method is important to ensure that the formation of metal oxide thin film is well defined and received according to demands. Parameters such as applied voltage and temperature play a significant role in moulding the outcomes, both morphologically and characteristics. Increase in applied voltage will result in the breakdown of the uniformed thin film, causing blisters and large pore sizes. This can be said as well for the increase in temperature during anodisation in terms of grain sizes. There is more room for improvement in the formation of gate oxide through anodisation so that it would have the most optimum feature for CMOS technology. For example, the oxide must be smooth, crack free and adhered to the substrate.

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