Chapter 4

ANODIC TITANIA MIM CAPACITORS

4.1 Introduction

Titanium oxide or Titania (TiO₂) is used for variety of applications such as gas sensors, photovoltaic devices and capacitors [Wisitsoraat et al., 2009, Gratzel, 2001, Chiang et al., 2005]. TiO₂ naturally exists in three crystalline phases namely rutile, anatase and brookite, with dielectric constant of 40 to 170 and energy bandgap of ∼3.0 eV [Mantzila and Prodromidis, 2005]. Recently, TiO₂ MIM capacitors have been fabricated using thermal oxidation [Chiang et al., 2005] and DC magnetron sputtering [Stamate et al., 2009]. Thermal oxidation and DC magnetron sputtering yield MIM capacitors with high leakage current density (> 10⁻⁴ A/cm²) and capacitance variation ΔC/C₀ of more than 10⁴ ppm [Chiang et al., 2005, Stamate et al., 2009]. This is due to the structural defects/traps available in bulk oxide and metal/insulator interface.

We have already fabricated MIM capacitor using barrier type anodic alumina and studied the electrical properties in previous chapter. Using electrode polarization model, it has been found that the low defect density and improved ionic polarization result a low VCC of 500 ppm/V and low leakage current density of 1nA/cm² at 2V. Unlike alumina, no report is available on fabrication and electrical characterization of MIM capacitor with anodic titania as per our knowledge. In this chapter, we explain the fabrication and characterization of the anodic TiO₂ MIM capacitors. The leakage mechanisms, frequency
dependency of capacitance and structural properties of these capacitors are studied in detail.

4.2 Fabrication process

Barrier type anodic titania with rutile and anatase crystalline phases were obtained by many authors using various aqueous electrolytes, such as ammonium pentaborate (bor-$H_2O$), sodium tetraborate [Habazaki et al., 2003, Vasil’eva et al., 2002]. Anodization of titanium using ammonium pentaborate in ethylene glycol (bor-gly) electrolyte were demonstrated by few authors [Gleaves et al., 1982, Soukup, 1972]. However, many authors have worked on anodization of aluminum with bor-gly electrolyte which results crystalline barrier oxide with low defect [Hickmott, 2007, Kannadassan et al., 2012b]. It has been observed that bor-gly solution results low leakage and high effective barrier height compared to bor-$H_2O$ [Hickmott, 2007]. This indicates that bor-gly electrolyte is a promising candidate for preparation of barrier type titania. In this paper, we have demonstrated the anodization of titanium using ammonium pentaborate dissolved in ethylene glycol to form MIM capacitors. To control the thickness of TiO$_2$, 15nm thick Ti was deposited over 100nm Al thin film. So at low anodization voltages, the Ti alone got anodized and the thickness of TiO$_2$ made constant.

The Al/TiO$_2$/Al structure was fabricated in the following manner. A bilayer of Ti/Al (15nm/100nm) was deposited using electron-beam evaporator with tungsten filament at a pressure of $8 \times 10^{-5} mBar$ over a 100nm thermally oxidized silicon dioxide on silicon (100) substrate. Here, Al acts as bottom electrode, which controls the thickness of TiO$_2$ during anodization. Ti film was potentiostatically anodized in a nonaqueous solution of ammonium pentaborate dissolved in ethylene glycol (20gl$^{-1}$) by the same size of platinum cathode. Electrolyte solution was prepared by adding 17gm of ammonium pentaborate (99% pure) for every 100ml of ethylene glycol. Anodization was done for anodization voltages of 10V, 15V and 20V till the current density reduced to $1 \mu A/cm^2$. To avoid etching of bottom electrode, only three quarters of sample area was dipped in the electrolyte. Once cleaned
thoroughly by deionised water, a 50nm thick Al top electrode was deposited on the anodized samples using thermal evaporator with the shadow mask area of \( \sim 0.61 \text{mm}^2 \). Fig. 4.1 shows the SEM cross section of all the three samples before top electrode deposition.

\section*{4.3 Performance of anodic titania MIM capacitors}

\subsection*{4.3.1 Formation and crystallization}

At higher anodization voltages (15V and 20V), the bottom Al electrode is also anodized. This forms a thin amorphous layer of \( \sim 2\text{nm} \) AlTiO (an alloy of both TiO\(_2\) and Al\(_2\)O\(_3\)) which stops the further migration of oxygen ions into Al electrode. Fig. 4.2 shows the depth profile of the three samples using secondary ion mass spectrometry (SIMS) in positive mode with 1kVCs. This shows ion distribution of Ti, Al, O, Si, Ti-O and Al-O. It is observed that the count of Al-O and Al is significant near TiO\(_2\)/Al interface which forms the AlTiO composite layer in T2 and T3 samples (Fig. 4.2 (b) and 4.2 (c)). But in T1 sample, it is not significant due to the lower anodization voltage (10V). The formation of AlTiO composite layer is due to outward migration of Al ions. However Al ions rapidly decrease
Figure 4.2: SIMS depth profile of all three samples (a) AV = 10V (b) AV = 15V and (c) AV = 20V.
Figure 4.3: X-Ray diffraction (XRD) spectra of anodized samples at various anodization voltages (a) 10V (b) 15V (c) 20V (A: Anatase, R: Rutile)

into TiO$_2$ region since it migrates slower than Ti ions [Habazaki et al., 2003]. This composite layer reduces the effective thickness of TiO$_2$ region. Fig. 4. 3 shows the XRD spectra of samples prepared at various anodization voltages. The spectra shows that the prepared TiO$_2$ at lower anodization voltage has crystalline phases of dominantly rutile with anatase and partially amorphous (Fig. 4. 3 (a)). At higher anodization voltages, the amorphous state is transferred to crystalline/quasicrystalline state (anatase). Outer layer of anodic film has amorphous structure (∼30%) which has been stabilized by ‘electrolyte derived species’ and a crystalline layer is available near bottom electrode [Habazaki et al., 2003].

Crystallization of anodic titania has been studied by many authors. Some of them reported that amorphous to crystalline transition occurs at low voltages (<10V) [Hourdakis and Nassiopoulou, 2010, Vasil’eva et al., 2002, Felske and Plieth, 1989]. H. Habazaki et al observed that during anodization the amorphous phase has been transformed to anatase [Hourdakis and Nassiopoulou, 2010]. According to M. S. Vasil’eva et al, borate and fluoride electrolytes have generally result in titania with rutile and anatase modifications respectively [Vasil’eva et al., 2002]. A. Felshe et al have reported that anodic titania shows rutile phases at low anodization voltages [Felske and Plieth, 1989]. Unfortunately, there are inconsistency found in the experimental conditions for TiO$_2$ crystallization such as

Crystallization process of anodic TiO$_2$ was addressed based on the observations of H. Habazaki et al and Piyus Kar [Habazaki et al., 2003, Kar, 2010]. The applied anodization field impacts the near insulator/metal interface with high energy. This forms a thin layer of rutile titania with bulk defect/bubbles (∼ 1nm) by inward migration of O$^{2-}$ ions [Habazaki et al., 2003, Kar, 2010]. Amorphous titania layer was formed over rutile layer by outward migration of boron ions [Habazaki et al., 2003]. After the formation of rutile, the inward migration of O$^{2-}$ ion was suppressed by the high field crystalline (high ionic resistivity) and anodized alumina regions. At this case, amorphous to anatase phase transition occurs at defect sites above rutile region at higher anodization voltages. The lower activation energy of bulk defects aids the heterogeneous nucleation of anatase titania [Kar, 2010]. Fig. 4. 4 shows the crystallization processes during anodization.

4.3.2 Capacitance and Voltage linearity

The capacitance and leakage current were measured using HP4155C semiconductor parameter analyzer. Fig. 4. 5 shows measured C-V characteristics of MIM Capacitors for 10 KHz at room temperature. It shows that the capacitance is increased about 2 fF/µm$^2$ for
higher anodization voltage which is due to improved crystalline property. Thin AlTiO layer acts as interfacial layer between TiO₂ and Al bottom electrode. This helps in formation of capacitance and reduction of leakage current [Phung et al.]. The linear (β) and quadratic (α) coefficients of capacitance are extracted using $C(V) = C_0 (\alpha V^2 + \beta V + 1)$, where $C_0$ is the capacitance at bias voltage of zero. Extracted $\alpha$ (ppm/V²) and $\beta$ (ppm/V) for various anodization voltages are shown in the inset of Fig. 5. Value of $\alpha$ reduces from 1431 to 938 ppm/V² as anodization voltage increases from 10V to 20V. High capacitance density and low VCC at high anodization voltage ensure the reduction of traps/defects at the bulk and metal/dielectric interface. The obtained $\alpha$ values are comparable to the earlier reports [Mondon and Blonkowski, Lee et al., Cheng et al., Wisitsoraat et al., Kannadassan et al., 2012b, Hourdakis and Nassiopoulou, 2010, Hickmott, 2007]. Recently it has been observed that VCC is inversely proportional to square of oxide thickness of MIM capacitor [Woo et al., 2012]. Therefore, one can reduce VCC and leakage current density as per recommendations of ITRS by increasing the thickness of anodic TiO₂.
4.3.3 Frequency dependence of capacitance

Fig. 4.6 shows the frequency dependent capacitance for various anodization voltages at 25°C. It is found that the capacitance is less sensitive to frequencies after 100KHz at higher anodization voltages, this indicates the stronger dipolar polarization is formed. We use Beaumont and Jacobs’s electrode polarization model to explain the dispersion of capacitance with frequency which is described in Chapter-3.

We have obtained the parameters of modified Beaumont and Jacobs model [Gonon and Vallae, 2007] by using measured capacitance $C$ and considering $\alpha = 0.5nm$, $\nu = 10^{12}Hz$, $L = 15nm$, $L_d \approx 0.9nm$ and interfacial energy barrier $E_i \approx 0.94eV$ for Al/TiO$_2$. We obtained the values of $\tau$, $N_t$ and $n$ for the best fit of various anodization voltages. These values are presented in Table. 4.1. It is observed that the defect density $N_t$ and factor $n$ are decreased as anodization voltage increases. Hence, sensitivity of the TiO$_2$ MIM capacitor to frequency reduces. Compatibility of the model and measured results are illustrated in Fig. 4.6.

According to L.M. Kosjuk et al [Kosjuk and Odynets, 1997], the second term of the model in Eq. 3.4 refers the contribution of relaxation polarization in formation of capacitance which is extracted using $(C - C_m)/C_m$ and shown in the inset of Fig. 4.6. This
<table>
<thead>
<tr>
<th>Sample name and $L_{\text{eff}}^{**}$</th>
<th>Measured $C$ (f$F/\mu\text{m}^2$) at 1V and 10KHz</th>
<th>Measured $\sigma$ ($\times 10^{-12}\text{S/cm}$) at 1V and 1MHz</th>
<th>Extracted Model Parameters</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 (T1), ~17nm</td>
<td>29.6</td>
<td>2.2</td>
<td>$4.4 \pm 2$</td>
<td>$3.72 \times 10^{-5}$</td>
</tr>
<tr>
<td>15 (T2), ~15nm</td>
<td>32.2</td>
<td>0.97</td>
<td>$6.1 \pm 2$</td>
<td>$1.17 \times 10^{-5}$</td>
</tr>
<tr>
<td>20 (T3), ~14nm</td>
<td>32.5</td>
<td>0.90</td>
<td>$8.6 \pm 2$</td>
<td>$1.01 \times 10^{-5}$</td>
</tr>
</tbody>
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Table 4.1: Measured and Extracted parameters of Anodic TiO$_2$ at various anodization voltages

* $AV$ - Anodization voltage  

** $L_{\text{eff}}$ - Effective thickness of TiO$_2$

4.3.4 Leakage characteristics and Temperature dependence

Figure 4.7: Measured leakage current density for all samples at room temperature

slowly varying term decreases in the order from 0.2 to 0.1. This reveals that the relaxation polarization is dominant at lower anodization voltages due to presence of large defects and slow relaxation time. At higher anodization voltages, the ionic polarization improves as amorphous state transferred to crystalline with low defect density. The modeling of ionic polarization of TiO$_2$ is presented in Chapter-6 in detail.

The leakage characteristics were measured by injecting electrons from Al bottom layer to TiO$_2$ layer (forward bias) and from top Al layer to TiO$_2$ layer (Reverse bias). Fig. 4. 7 shows the measured leakage current density of all the samples at room temperature for different
Figure 4.8: Measured leakage current density at various temperatures for T3 sample

applied voltages and Fig. 4.8 shows the measured leakage current density of sample T3 at various temperatures for different applied voltages. It is observed that the I-V characteristics obtained is asymmetric. This is due to non-uniform crystalline structure and anodization of Al (AlTiO) which result in different effective barrier heights at the top Al/TiO$_2$ and bottom TiO$_2$/Al interfaces. Also it is clear that leakage current is more sensitive to temperature in forward bias than reverse bias. To explain these properties of anodic TiO$_2$, conduction mechanisms such as Schottky emission (SE) and Poole-Frenkel (PF) emission are studied.

In Fig. 4.7, higher slope till 0.3V indicates the SE tunnelling of electrons to the unoccupied defect or trap states near metal insulator interface. Moderate fields, between 0.3V to 1V, are dominated by PF tunnelling emission mechanism, where the trapped electrons enhance from defect states to conduction states of the dielectric. After 1V, Poole-Frenkel saturation is observed. This is due to the trap barrier height is reduced to zero at higher fields, thus the charged (coulombic) traps have no effect on the carriers [Southwick III et al., 2010]. According to [Chakraborty et al., 2005], the expression for leakage current density due to SE and PF mechanisms are expressed as,

$$J_{SE} = A_R T^2 \exp \left\{ -\frac{1}{kT} \left( q\phi_B - \beta_{SE} \sqrt{E} \right) \right\}$$  \hspace{1cm} (4.3.1)

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Figure 4.9: Extracted barrier height for T3 sample at various temperatures. (a) Forward bias, (b) Reverse bias, (c) Forward bias at $E_{V}=0.1V$, $E_{V}=1V$, (d) Reverse bias at $E_{V}=0.1V$, $E_{V}=1V$.

$$J_{PF} = C E \exp \left\{ -\frac{1}{\xi kT} \left( q\phi_{PF} - \beta_{PF} \sqrt{E} \right) \right\}$$

(4.3.2)

where $A_R$ is Richardson’s constant ($= 1200 cm^{-2} k^{-2}$) and $C$ is proportionality constant. $\phi_B$ and $\phi_{PF}$ are schottky barrier and trap barrier heights respectively, and $E$ is applied electric field. The constant $\beta_{SE}$ and $\beta_{PF}$ are expressed as $\beta_{SE} = \left( q^3 / 4\pi \varepsilon_0 \varepsilon_r \right)^{1/2}$ and $\beta_{PF} = \left( q^3 / \pi \varepsilon_0 \varepsilon_r \right)^{1/2}$, where $\varepsilon_0$ is permittivity of the free space and $\varepsilon_r$ is dielectric constant of the insulator. The dielectric constant, $\varepsilon_r$ can vary from 40 to 120 depending on crystalline property and structural defects. We have considered it as 60 due to the presence of amorphous layer and rapid degradation of capacitance with frequency. Barrier height is extracted as a function of applied electric field $E$ for various temperatures using Eq. 4.3.1. Fig. 4.9 (a) and 4.9 (b) show the extracted barrier height for T3 sample (anodized at 20V) at forward and reverse bias respectively. As expected, a small difference of 0.05eV in
barrier height at bottom Al/TiO$_2$ and top Al/TiO$_2$ interface is observed at low fields. This confirms the formation of AlTiO at bottom electrode interface which considerably reduces the overall leakage.

Fig. 4. 9 (c) and 4. 9 (d) show the extracted barrier heights for various temperatures at applied voltages 0.1V and 1V. Compared to reverse bias, a large change in barrier height is observed for increase in temperature at forward bias (bottom injection). It shows that crystalline TiO$_2$ region and interface is sensitive to temperature. A recent similar observation is presented for atomic layer deposition (ALD) of TiO$_2$ in MIM capacitor [Seo et al., 2011]. Barrier height reduction with temperature increment can be explained with the observations of T. W. Hickmott in anodized Al$_2$O$_3$ thin film [Hickmott, 2005]. It was
concluded that effective tunnelling barrier of the empty traps has largely decreased due to increase in temperature [Hickmott, 2005].

To study further, PF tunnelling mechanism is used to extract the trap barrier heights at various temperatures for forward and reverse bias. From the temperature dependent leakage characteristics of Fig. 4. 8, \( \ln(J/E) \) vs. \( 1/T \) plot is drawn for forward bias and shown in Fig. 4. 10 (a). Using this plot, trap barrier height is extracted at specified fields at different temperature which is shown in Fig. 4.10 (b). The intrinsic trap barrier height is obtained by extrapolating the obtained curves to zero field [Yeh et al., 2007]. Similar procedure is followed to extract trap barrier height in reverse bias and shown in Fig. 4. 10 (c) and 4. 10 (d). It is clear that traps available near to bottom electrode (in crystalline region) are more sensitive to temperature where traps in amorphous region are stable. It is observed from Fig. 4. 10 (b) that intrinsic trap barrier height (at \( E^{1/2} = 0 \)) of crystalline region (near bottom electrode) is largely degraded with increase in temperature. At reverse bias, the amorphous region shows a trap barrier height of \(~0.15\text{eV}\) which is stable with temperature. The partial crystalline structure of anodic TiO\(_2\) and interfacial layer cause asymmetric leakage/breakdown at positive and negative half cycle. In a big wafer level anodization, there is a possibility of non-uniform oxide thickness due to unequal cathode size with wafer or/and non-uniform anodic field distribution. This may lead to undesirable effects in circuit level, however, it is purely a statistical impact. Process variations can be studied in detail with respect to anodization voltage, electrolyte composition and temperature.

4.3.5 Anodization with various electrolytes: A comparison

Anodic TiO\(_2\) MIM capacitor with two electrolytes

A 100nm SiO\(_2\) insulating structure has grown over Si substrate by thermal oxidation at 1200\(^\circ\)C in dry O\(_2\). Over SiO\(_2\), a bilayer thin film of 15nm Ti on 100nm Al is deposited using electron beam evaporator with tungsten filament at a pressure of \(8 \times 10^{-5}\)\text{mBar}. Set of samples, named Ti-1, have been anodized in a solution of ammonium pentaborate (APB)
Figure 4.11: XRD spectra of both samples (a) Ti-1 and (b) Ti-2 dissolved in ethylene glycol (20gL⁻¹) at anodization voltage of 20V till current density reduces to 1µA/cm². Electrolyte solution was prepared by adding 17gm of APB for every 100ml of ethylene glycol. Remaining samples, Ti-2, were anodized in similar condition using solution of 1M sulfuric acid. Both samples are anodized by platinum cathode of equal size as anode to maintain uniform thickness. While anodization, the samples are dipped only three quarters of total area to avoid etching for the bottom electrode. After anodization, the samples were cleaned thoroughly by deionized water. Finally, Al film of 50nm was deposited by thermal evaporation through a shadow mask area of 0.61mm². Fig. 4. 11 shows the XRD spectra of the surfaces of both the anodized samples at 20V. Spectra show that the sample Ti-2 is rutile. At the same time, spectra of sample Ti-1 shows peaks for anatase and rutile TiO₂.

Fig. 4. 12 shows the measured C-V characteristics of anodic TiO₂ MIM capacitor for 100 KHz at room temperature for both samples. It can be observed that sample Ti-1 shows higher capacitance density (33fF/µm²) than that of Ti-2 (26fF/µm²). This is due to improved crystalline of anodized TiO₂ by APB. The quadratic (α) and linear (β) coefficients of capacitance are extracted and shown in the inset of Fig. 4. 12. It is observed that sample Ti-1 coefficient values are low for sample Ti-1 compared to Ti-2, this is due to
Figure 4.12: C-V characteristics of anodic TiO$_2$ MIM capacitors for 100 KHz at room temperature. Inset: Extracted quadratic ($\alpha$) and linear ($\beta$) coefficients of capacitance for both samples.

Figure 4.13: $(C - C_m)/C_m$ as function of frequency for both the samples. Low traps/defects at metal/dielectric interface and bulk. This ensures that the formation of electrode polarization is more effective in Ti-1, this may be due to the uniform and slow growth of anodic oxides using APB.

Fig. 4.15 shows the normalized capacitance, $(C - C_m)/C_m$ as function of frequency for both the samples. $C_m$ is the capacitance for no electrode polarization, expressed as $C_m = \varepsilon_0\varepsilon_rS/L$, with top electrode area $S$ and oxide thickness $L$. A large change, about 50%, in capacitance from low to high frequency has been observed in Ti-2. Particularly, the fast reduction in capacitance at low frequency ensures the poor ionic polarization, this is due to the slow time constant of traps or oxygen vacancies. Saturation of capacitance is observed.
The measured leakage current density is shown in Fig. 4.14 for both the samples. The sample Ti-1 and Ti-2 show the leakage current density of \(3.97 \times 10^{-6} \text{A/cm}^2\) and \(3.67 \times 10^{-5} \text{A/cm}^2\) at 1V respectively. This ensures that the barrier height of TiO\(_2\) has been enhanced by APB solution. On the other hand, J-V characteristics of both the samples are asymmetric in nature. This is due to the non-uniform effective barrier height at top and bottom metal/dielectric interface. To analyze this behavior, Schottky emission mechanism is used to extract barrier heights for both samples. Barrier height is extracted as a function of applied electric field \(E\) for both samples using Eq. 4.3.1. Extracted barrier heights for forward and reverse biases are shown in Fig. 4.15 (a) and (b) respectively. The effective barrier height can be estimated by extrapolating the low field region to reach field \(E = 0\).
line. It is observed that the barrier height is enhanced about 0.03eV for sample anodized using APB. But in reverse bias, such enhancement is not observed.

4.4 Summary

Our TiO\textsubscript{2} MIM capacitors using anodic oxidation show a high capacitance density of 33\textit{fF/µm}\textsuperscript{2}, and low leakage current density of 9.61 \times 10^{-8} A/cm\textsuperscript{2} at 1V. It is observed that crystalline and polarization properties are improved at higher anodization voltages, which reduce the VCC and sensitivity of the capacitance with frequency. The crystallization of anodic titania is discussed in detail. The asymmetric leakage characteristics in forward and reverse bias were studied using Schottky emission and Poole-Frenkel emission mechanisms. It is observed that the trap barrier height at top electrode interface is deeper than that of bottom electrode interface. This is due to anodization of bottom Al electrode which form AlTiO layer. This layer helps in formation of capacitance and reduce the leakage current density. From the obtained results of anodic alumina, titania MIM capacitors indicate that the anodization has large potential to solve many issues in high-\textit{k} dielectric oxidation. Anodic oxidation of barrier type oxides opens an effective low cost fabrication of high density MIM capacitor for future RFICs and MMICs.