國立交通大學

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原子層沉積二氧化鋯/三氧化二鋁於砷化銦鎵金氧半 電容之電性與表面化性分析的研究

Investigation of Electrical and Interfacial Chemistry Analyses for Atomic-Layer-Deposition ZrO₂/Al₂O₃/In_{0.53}Ga_{0.47}As MOSCAPs

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原子層沉積二氧化鋯/三氧化二鋁於砷化銦鎵金

氧半電容之電性與表面化性分析的研究

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在此篇論文初,我們研究了利用原子層沉積系統的前驅物做表面的預處理, 像是 TMA 以及 TEMAZ。然而,與 TEMAZ 相比,我們發現 TMA 表面處理可 以有效地抑制聚積區的頻率分散與空乏區的介面缺陷電荷。為了更進一步探討二 氧化鋯/砷化銦鎵的介面與開極氧化層的特性,我們使用了不同的後沉積退火溫 度及氮氫混合氣體退火。此外,藉由 TMA 預處理,我們在二氧化鋯與砷化銦鎵 的介面併入數層的三氧化二鋁,並且討論其表面特性。從數據分析上指出電容在 每個不同的三氧化二鋁層條件下,後沉積退火溫度 300 度及氮氫混合氣體退火展 現最好的電性。另外,我們利用電導法來萃取介面缺陷電荷密度;仍然可以觀察 到在 PDA 溫度 300 度及 FGA 下能隙深處 (midgap) 的缺陷電荷是最低的。在 XPS 分析的證明下,我們推測這個結果可能是在電容介面上有較高的 As²⁺/As₂O₅、 As₂O₃/As₂O₅、In₂O₃/InAsO₄。此外,從電性與表面化學特性來看,我們可以證實 較厚的三氧化二鋁夾層可以改善介面品質。 最後,我們建立了一個分佈模型來解釋操作在聚積區之半導體表面與閘極氧 化層內缺陷的穿隧機制。然後我們利用模型與實驗數據做媒合並且定量地萃取閘 極介電層內的缺陷密度。而與前面的結果相比有很好的一致性。



Investigation of Electrical and Interfacial Chemistry Analyses for Atomic-Layer-Deposition ZrO₂/Al₂O₃/In_{0.53}Ga_{0.47}As MOSCAPs



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ABSTRACT

In the beginning of this thesis, we have investigated the surface pretreatment before depositing gate dielectric by using the precursors of ALD system, such as TMA and TEMAZ. However, compared to TEMAZ, we find the TMA surface treatment is effective to suppress the frequency dispersion and interface states in accumulation and depletion region. In order to further discuss the interface and gate oxide property of ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs, we apply various post-deposition annealing temperatures with forming gas annealing (FGA). Moreover, by TMA pretreatment, we incorporate several Al₂O₃ inter-layers with the interface of ZrO₂ and In_{0.53}Ga_{0.47}As and discuss their interface properties. It is noted that the MOSCAPs under PDA 300 °C with FGA show the best electrical characteristics at each Al₂O₃ inter-layer conditions. In addition, we utilize the conductance method to extract the density of interface states and still observe that the D_{it} exists near midgap is the lowest at PDA 300 °C with FGA. With the evidence of XPS analysis, we suppose that the result might be caused by higher amounts of the As^{2+}/As_2O_5 , As_2O_3/As_2O_5 , and $In_2O_3/InAsO_4$ at the MOSCAPs interface. Furthermore, from the electrical and interfacial chemistry characteristics, we demonstrate that the interface quality could be improved with thicker Al_2O_3 inter-layer.

Eventually, we establish a distributed model to explain the tunneling mechanism between the semiconductor surface and trap states in the gate oxide which is biased in accumulation region. And we fit the experimental data with the model and quantitatively extract trap states density of the gate dielectric. As comparing with the aforementioned results, they are in good consistency.



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學生生涯終究還是結束了。回想起這兩年多的碩士生活,不禁覺得時間真的 過得很快,有種淡淡的哀傷。在研所期間遇到的人事物現在回想起來依然歷歷在 目,首先要感謝我的指導教授簡昭欣老師,謝謝您總是在研究方面給予我們支持 與協助,更提供很好的學習與實驗環境,讓我們能確實的學習到專業知識,在待 人處事上也常提醒我們哪些地方是該注意並改進的,使我們在前進職場的道路上 能懂得應對得體。很高興能在研究所期間選擇老師指導,使我在未來的人生道路 上提前學到了不少寶貴經驗。

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Chapter 1

Introduction

1.1 General Background

Recently, in order to maintain the performance of silicon-based metal oxide semiconductor field-effect-transistors (MOSFETs) and scale the size of transistors at the same time, the gate dielectric thickness and channel length have been reduced to support this criterion. However, when the reduction of device dimensions is approaching physical limitation, high-k materials and high mobility channel substrates have been developed to remain or improve the performance. Therefore, several bulk materials, such as Ge, GaAs, InGaAs, and InAs [1] have attracted much attention as the potential candidates due to their higher electron mobility than Si, as shown in Table 1.1. From Fig. 1.1, we can find various integration and applications of Ge/ III-V channel materials on Si platform [2]. The CMOS device fabricated on the non-Si channel materials which accord with the More Moore approach are pursuing for the high driving current. As a result, III-V materials are used to be n-channel MOSFETs, and Ge is proper for n- or p-channel MOSFETs. Furthermore, if III-V p-channel MOSFETs are expanded as practical structures, III-V or Ge CMOS might be appropriate development in the future. In addition, high-k materials have been regarded as replaceable gate dielectrics for scaling problems and insulator leakage issues of conventional SiO₂. With comparing to silicon dioxide, high-k materials can provide the higher capacitance without reducing oxide thickness and increasing gate leakage current. So far, there are numerous literature demonstrate that the MOSFETs developed as the potential devices, such as Ge [3], InGaAs [4,5] channels by using high-k gate dielectrics. Nevertheless, the interface characteristics between gate oxide and III-V semiconductors still exist important issues, such as Fermi-level pinning and an amount of interface states. Thus, there are several solutions have demonstrated to passivate the interface and prevent Fermi-level pinning [4,6-9]. With solving these problems, high-k/III-V MOSFETs will be one of the promising structures in the future.

1.2 Motivation

To understand III-V compound semiconductors used to fabricate MOSFETs, there are many technological challenges need to be conquered. One of the main obstacles is the gate dielectrics which lack high oxide quality, thermodynamic stabilization, low leakage current, high breakdown fields, and excellent native oxide like SiO₂ on Si naturally. Moreover, III-V surface exists such as vacancies, defects, or incomplete dimerization which cause unsaturated bonds and form electrically active traps [10,11]. Thus, high interface trap densities might give rise to insufficient Fermi-level response, preventing control over the charge carriers in the channel [12], the degradation of the drive current, and the subthreshold swing. For that reason, the interfacial control in III-V gate stack is strongly needed for realizing low D_{it}. To develop appropriate gate dielectrics and better interface properties, forming a stable interface with suitable thermal budget and how to reduce the density of interface states (D_{it}) are the important issues. In particular, fabricating good interface qualities between III-V and high-kdielectrics are extremely challenging. Here, we will use In_{0.53}Ga_{0.47}As as our substrates, Al₂O₃ and ZrO₂ as gate oxide to study their interface and oxide characteristics.

1.3 Organization of the Thesis

In Chapter 1, an introduction of the background and the main challenges has been realized. We also describe the problems of gate dielectric quality and interface state issues.

In Chapter 2, in order to investigate the property of the ZrO_2 oxide quality and the high-k/III-V interface, the frequency dispersion at accumulation region, the hysteresis, and conductance method are extracted from the measured C-V electrical characteristics and the XPS analysis to confer the interfacial chemistry. First, we utilize the various pretreatment to passivate the high-k/In_{0.53}Ga_{0.47}As interface before depositing gate dielectrics. Then, incorporating several Al₂O₃ as inter-layer between ZrO₂ and In_{0.53}Ga_{0.47}As is demonstrated. Furthermore, we discuss the influence of various PDA conditions with FGA.

In Chapter 3, we apply the distributed border traps model to quantitatively determine the density of bulk-oxide traps extracted from our measured capacitance and conductance data. And we compare these N_{bt} values with the frequency dispersion ΔC in Chapter 2.

In Chapter 4, we make a conclusion as the aforementioned results and give some -100 suggestions for future works.

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Fig. 1.1 Possible evolution scenario for III-V/Ge devices on Si platform through heterogeneous



	Si	Ge	GaAs	In _{0.53} Ga _{0.47} As	InAs			
Lattice constant (Å)	5.431	5.646	5.653	5.869	6.058			
Band gap (eV)	1.12	0.66	1.42	0.74	0.36			
Intrinsic carrier conc. (cm ⁻³)	9.6×10 ⁹	2.4×10 ¹³	2.2×10 ⁶	6.3 ×10 ¹¹	1×10 ¹⁵			
Effective conduction band density of states (cm ⁻³)	2.8×10 ¹⁹	1.04×10 ¹⁹	4×10 ¹⁷	2.2×10 ¹⁷	8.7×10 ¹⁶			
Effective valence band density of states (cm ⁻³)	1.04×10 ¹⁹	6×10 ¹⁸	9.7×10 ¹⁸	7.8×10 ¹⁸	6.6×10 ¹⁸			
Electron mob. (cm ² /Vs)	1600	3900	9200	12000	40000			
Electron	m _t : 0.19	m _t : 0.082	0.067	0.043	0.023			
mass (/m ₀)	m _l : 0.916	m _l : 1.467						
Hole mob. (cm ² /Vs)	430	1900	400	300	500			

Table 1.1 Material properties of bulk Si, Ge, GaAs, $In_{0.53}Ga_{0.47}As$, and InAs at 300K

Chapter 2

Studies of $ZrO_2/Al_2O_3/In_{0.53}Ga_{0.47}As$ MOSCAPs with Electrical Characteristics and Interfacial Chemistry

2.1 Introduction

Recent research shows III-V compound semiconductor has been actively investigated to replace the Si-based CMOS technology for pursuing higher device performance and lower power consumption due to their high electron mobility, high saturation velocity, and small electron effective mass [1-3]. However, the obstacle for the implementation of III-V semiconductors is the high density of interface states (D_{it}) which has caused Fermi level pinning between gate dielectric and III-V interface [4]. To improve the device performance, it's important to reduce the D_{it} at the III-V interface, which results in increasing gate leakage current, lower drive current and sub-threshold swing [5-6]. Several researches such as combination of high-k dielectric materials, crystal orientations, appropriate deposition conditions, and various passivation techniques have shown in recently [7-10]. Moreover, previous publication revealed that in order to reduce the native oxide on III-V surface and improve electrical characteristics, there have developed various treatment or passivation methods such as ammonium sulfide passivation before oxide deposition [11], effect of hydroxylation on the interface [12]. In addition, depositing gate dielectric by atomic-layer-deposited (ALD) can also reduce native oxide and interface states because of the "self-cleaning" effect by ALD precursors on III-V semiconductors such as GaAs [13-14], InGaAs [15-17].

With continuous downscaling of gate dielectrics, developing high-k materials such as Al₂O₃ [18], and HfO₂ [19], ZrO₂ [20-23] with low interfacial density of states and low gate leakage current is important for III-V semiconductors as a high mobility channel material. Al₂O₃/InGaAs MOS interfaces formed by using ALD are known to have the better quality, but the dielectric constant is still not enough to provide the high performance devices [5]. On the other hand, HfO₂ and ZrO₂ [24-27] have attracted much attention as promising gate dielectrics of III-V semiconductors because of the high permittivity. In addition, ZrO₂ dielectric constant value is higher than HfO₂ [28] as shown in Fig. 2.1 but lower band offset shown in Table 2.1. However, the high-k/III-V interfacial property is complicated due to the more number of elements present at the interface when compared to the Si/SiO₂. When exposure to the air, the native oxides of In_{0.53}Ga_{0.47}As influence the high-k/III-V interface by increasing the leakage current and density of interface states between the gate dielectrics and the III-V substrate [29]. Therefore, there were some efforts show that the Trimethylaluminium (TMA, Al(CH₃)₃) of ALD precursors can be used to remove native oxides on III-V surface[14,30], but the influence of Tetrakis(ethylmethylamino) zirconium [TEMAZ, $Zr(N(C_2H_5)(CH_3))_4]$ of the ALD precursors as pre-deposition treatment hasn't been studied.

In our work, we will use the TEMAZ and TMA precursor to be pre-deposition treatment before depositing ZrO_2 . Nevertheless, compared with the aforementioned pretreatment, the $ZrO_2/In_{0.53}Ga_{0.47}As$ interfaces still have worse properties. For this reason, we will insert Al_2O_3 inter-layer to improve the $ZrO_2/In_{0.53}Ga_{0.47}As$ interface quality. Besides, there is several researches show that annealing with hydrogen could reduce the oxide charge and interface states and the presence of thermal energy can reconstruct the bonds and passivate dangling bond all over the gate oxide [31, 32]. On behalf of further improving oxide interface quality, various post-deposition annealing conditions with FGA have been implemented. Finally, we will discuss the influence of the various pretreatment and inserting Al_2O_3 inter-layers by electrical characteristics and interfacial chemistry. In this chapter, capacitance-Voltage (C-V) and conductance-voltage (G-V) characteristics were measured by HP4284A *LCR* meter at the temperature of 300K.

2.2 Experimental Procedures of In_{0.53}Ga_{0.47}As MOSCAPs

2.2.1 Various Surface Pretreatment and Capacitor Fabrication

The MOS capacitor substrates prepared in this thesis were p-type InP (100) wafers with Zn-doped and doping concentration of ca. 1×10^{18} cm⁻³ as the bulk substrates. Then, growing thickness of 300 nm p-type In_{0.53}Ga_{0.47}As (100) with Zn-doped and doping concentration of ca. 1×10¹⁸ cm⁻³ as a buffer layer and 60-nm p-type In_{0.53}Ga_{0.47}As (100) with Zn-doped and doping concentration of ca. 1×10^{16} cm⁻³ as a channel layer. Before depositing gate dielectric, there must be a thin native oxide layer on the wafer's surface. In order to remove this, there were three clean steps prior to gate dielectric deposition. At first, the sample was rinsed in acetone (ACE) for 5 minutes. Next, rinsing in isopropanol (IPA) for 5 minutes, followed by dipping in deionized water (D.I. water). Finally, rinsing in dilute HCl solution (HCl : H₂O=1:10) for 2 minutes. Then the samples were loaded into ALD chamber. Tetrakis(ethylmethylamino) zirconium [TEMAZ,Zr(N(C₂H₅)(CH₃))₄] or trimethylaluminum [TMA, Al(CH₃)₃] precursor pulses were performed for 10 cycles as surface pretreatment. After that, the treated In_{0.53}Ga_{0.47}As surfaces were *in-situ* grown the ZrO₂ thin film for 80 cycles by atomic-layer-deposition (ALD) system at 250 °C. After depositing, different annealing conditions such as 300 °C, 400 °C, and 500 °C for 120 s in N₂ ambience have been tested. Then, we defined the capacitor area by photolithography and patterning gate electrode by sputter system of 100 Å of Ti and 500 Å of Pt. The capacitor area of gate electrode was ca. 1×10^{-4} cm² by optical microscopy. Backside contacts were also formed by sputter system (Ti/Pt : 100 Å/500 Å). Finally, all of the samples were prepared by forming gas annealing (FGA) at 250 °C for 30 min in a 10% $H_2/90\%$ N₂ ambience.

The process flow and structure are shown in Fig. 2.2 and Fig. 2.3.

2.2.2 Incorporating Several Cycles of Al₂O₃ with ALD-TMA /ZrO₂ Growth and Capacitor Fabrication

The MOS capacitor substrates prepared in this thesis were p-type InP (100) wafers with Zn-doped and doping concentration of ca. 1×10^{18} cm⁻³ as the bulk substrates. Then, growing thickness of 300 nm p-type In_{0.53}Ga_{0.47}As (100) with Zn-doped and doping concentration of ca. 1×10^{18} cm⁻³ as a buffer layer and 60-nm p-type In_{0.53}Ga_{0.47}As (100) with Zn-doped and doping concentration of ca. 1×10^{16} cm⁻³ as a channel layer. Before depositing gate dielectric, there must be a thin native oxide layer on the wafer's surface. In order to remove this, there were three clean steps prior to gate dielectric deposition. At first, the sample was rinsed in acetone (ACE) for 5 minutes. Next, rinsing in isopropanol (IPA) for 5 minutes, followed by dipping in deionized water (D.I. water). Finally, rinsing in dilute HCl solution (HCl:H₂O=1:10) for 2 minutes. Then the samples were loaded into ALD chamber. Trimethylaluminum [TMA, Al(CH₃)₃] precursor pulses were performed for 10 cycles as surface pretreatment. After that, the different cycles (1, 5, 10 cycles) of Al₂O₃ and 80 cycles ZrO₂ thin film were grown by atomic-layer-deposition (ALD) system at 250 °C. After depositing, different annealing conditions such as as-deposited, and 300 °C, 400 °C, and 500 °C for 120 s in N₂ ambience have been tested. Then, we defined the capacitor area by photolithography and patterning gate electrode by sputter system of 100 Å for Ti and 500 Å for Pt. The capacitor area of gate electrode was ca. 1×10^{-4} cm² by optical microscopy. Backside contacts were also formed by sputter system (Ti/Pt : 100 Å/500 Å). Finally, all of the samples were prepared by forming gas annealing (FGA) at 250 $^\circ C$ for 30 min in a 10% H_2 / 90% N_2 ambience.

The process flow and structure are shown in **Fig. 2.4** and **Fig. 2.5**. The cross-sectional TEM image of as-deposited TMA/Al₂O₃ 10 cycle/ZrO₂ on $In_{0.53}Ga_{0.47}As$ channel layer with FGA is shown in **Fig. 2.6**.

2.3 Capacitor Characteristics and Interfacial Chemistry of ALD-ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs with Various

Pretreatments

In the multi-frequency *C-V* curves, we can see the dispersion among different frequencies at the accumulation and depletion region, respectively. Consequently, we quantitatively define the frequency dispersion ratio ΔC at the accumulation region as follows: $\Delta C (@V_g = -2 V) \equiv \{[C(@100Hz) - C(@100kHz)]/C(@100kHz)\} \times 100\%$ (2.1) Here, ΔC is the frequency dispersion of the capacitance measured in 100 kHz and 100 Hz at $V_g = -2 V$. The overviews of all the samples in capacitance frequency dispersion are shown in **Table 2.2**.

The hysteresis curve in *C-V* measurement is observed at 100 kHz with two sweep directions; one is from the accumulation to inversion region and the other one is opposite. Therefore, we determine V_{FB} experimentally by plotting $(1/C_{hf})^2$ versus V_g , respectively. Then differentiating these two curves and finding the sharply peaked curves whose peaks mean the flatband voltage V_{FB} (not shown). The different values between these two peaks are about V_{FB} shift or hysteresis. The overviews of all the samples in hysteresis (V) are shown in **Table 2.3**.

2.3.1 C-V and G-V properties of MOSCAPs under Various Post-Deposition Annealing Conditions w/FGA

Fig. 2.7 (a) (b) (c) and Fig. 2.9 (a) (b) (c) show the multi-frequency C-V curves of p-type In_{0.53}Ga_{0.47}As MOSCAPs with ZrO₂ gate dielectric for TEMAZ or TMA pretreatment with FGA under different PDA conditions, respectively. For TEMAZ treatment, the thermal condition with PDA 300 °C for 120s demonstrates the best C-V electrical characteristics than the others. Though the capacitance at V_g = -2 V is the lowest (Fig. 2.7 (a)), the frequency dispersion near accumulation region with PDA 300 °C ($\Delta C = 99.4\%$) is better than the others $(\Delta C = 160.9\% \text{ at } 400 \text{ }^{\circ}C \text{ and } \Delta C = 129.5\% \text{ at } 500 \text{ }^{\circ}C)$, are shown in **Table 2.2**. The huge hump at all the samples from V_g = -0.5 V to V_g = 0.5 V indicate the response of interface states. Then, from Fig. 2.8 (a) (b) (c), we can find the color variation of conductance maps from V_g = -1 V to V_g = -2 V is becoming dramatic when above PDA 400 °C from low toward high frequency. We suppose this phenomenon to the border traps response of gate dielectrics. Catching more attention to these maps, we can observe the concentric circles between V_g = -1 V and V_g = 0 V. It might indicate the movement of Fermi level from high positive gate voltage to this region and pinned between 1 kHz and 10 kHz. Then toward high negative gate voltage, the voltage will drop on the gate dielectrics. Besides, there is an additional signal at high frequency with high negative gate voltage as the increasing temperature of PDA, this might be the energy loss. And a distinct map signal exists from $V_g = 1$ V to $V_g = 2$ V at low frequency region might be the interface traps response accompanying with minority carrier signal, especially at PDA 500 °C.

Moreover, for TMA treatment from Fig. 2.9 (a) (b) (c), we can also observe the frequency dispersion near accumulation region with PDA 300 °C ($\Delta C = 42.7\%$) is better than the others ($\Delta C = 84.3\%$ at 400 °C and $\Delta C = 75.9\%$ at 500 °C), also shown in Table 2.2. The hump from V_g= -0.5 V to V_g= 0.5 V indicate the density of interface states is lowest at PDA

300 °C. Furthermore, we extract the hysteresis from the difference of V_{FB} and find PDA 300 °C with FGA has the lowest oxide traps or interface states, are shown in **Table 2.3**. And then, from **Fig. 2.10 (a) (b) (c)**, there is obvious variation of contours from V_g = -1 V to V_g = -2 V as the increasing temperature of PDA and these might be the presence of oxide traps. As well Fermi level pinning also occur between V_g = -1 V and V_g = 0 V among 1 kHz and 10 kHz. In addition, the energy loss exists at high frequency with high negative gate voltage when the temperature of PDA increases. Similarly, the response of interface states and minority carrier also exists at gate voltage between 1 and 2 volts, especially at PDA 500 °C.

2.3.2 Comparison of Various Pretreatments on Electreical and Interfacial Chemistry Characteristics

From Fig. 2.7 to Fig. 2.10, we can notice that the frequency dispersion near accumulation region of TMA treatment is much weaker and the hysteresis is smaller than TEMAZ, especially at PDA 300 °C, which reveals the high-k dielectrics and interface quality are improved. In general, the frequency dispersion and the hysteresis of the C-V curves are mainly caused by the existence of border traps and interface states. Therefore, we infer that the interface between gate dielectric and substrate might be repaired by TMA pretreatment. This phenomenon means TMA treatment is better than TEMAZ. In order to further interpret the interface property, we select specific condition to analyze the discrepancy of chemical characteristics as follows.

The top two graphs of **Fig. 2.36** (a) (b) (c) show X-ray photoelectron spectroscopy of ALD-TEMAZ or TMA 10 cycle /ZrO₂ 10 cycles on p-type In_{0.53}Ga_{0.47}As with FGA at PDA 300 °C. XPS spectra were taken by Ga $2p_{3/2}$, In $3d_{5/2}$, and As $2p_{3/2}$ core levels. From **Fig. 2.36** (a), there is no obvious variation in Ga $2p_{3/2}$ spectra. However, the In $3d_{5/2}$ and As $2p_{3/2}$ spectra, shown in **Fig. 2.36** (b) (c), indicate the existence of In- and As-oxide in both

samples. **Table 2.6** shows the ratio of the fitted area such as In_2O_3 to $InAsO_4$ from In $3d_{5/2}$ spectra, As^{2+} to As_2O_5 and As_2O_3 to As_2O_5 from As $2p_{3/2}$ spectra. From the area ratio, we can demonstrate that the higher ratio value is, the better electrical characteristic is, which is consistent with aforementioned conclusion. This finding confirms the TMA treatment might prevent or reduce the presence of inferior substrate native oxides at the interface before depositing gate dielectric [33].

2.4 Capacitor Characteristics of ALD-ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs with inserting Al₂O₃ Inter-layer

The foregoing section indicated that using TMA precursor has a self-cleaning effect before depositing ZrO₂. However, from above electrical and interface chemical characteristics, the ZrO₂/In_{0.53}Ga_{0.47}As interfaces still have inferior quality than Al₂O₃ or HfO₂/In_{0.53}Ga_{0.47}As [34]. For the purpose, we will incorporate several Al₂O₃ inter- layers with ALD-TMA/ZrO₂ to confer its interface property.

2.4.1 *C-V* and *G-V* properties of MOSCAPs under Various Post-Deposition Annealing Conditions w/FGA

At first, we desire to discuss inserting Al₂O₃ for 1cycle into ALD-TMA/ZrO₂ interface to confer the oxide and In_{0.53}Ga_{0.47}As interfacial electrical property with FGA under various PDA conditions. From **Fig. 2.11** (a) (b), comparing the samples with or without PDA 300 °C condition after FGA, we can find that both samples have not reached strong accumulation, which may indicate high interface states close to the valence band edge. From the frequency dispersion in **Table 2.2** and the hysteresis in **Table 2.3**, the PDA 300 °C (Δ C=41.7%,

 $\Delta V=0.44 \text{ V}$) is both smaller than as-deposited one ($\Delta C=43.4\%$, $\Delta V=0.49 \text{ V}$). Then, from Fig. 2.11 (b) (c) (d), Table 2.2, and Table 2.3, also display the PDA 300 °C have better properties than the others. Moreover, the C-V characteristics show that the hump between $V_g=-0.5 \text{ V}$ and $V_g=0.5 \text{ V}$ is getting larger as the PDA temperature increase, which may exhibit more response of D_{it}. Therefore, we can speculate that the superior temperature of post deposition annealing might be 300 °C for our substrates. The conductance contour from Fig. 2.12 (a) (b) (c) (d) at low frequency, it might indicate the existence of border traps with high negative V_g . And the color variation around 0 V to high positive V_g are becoming noticeable above PDA 400 °C, we suppose that these might be interface traps accompanying with minority carrier signal rather than only minority carrier response [35].

Continued from the preceding paragraph, the quality of ALD-TMA/Al₂O₃ 1cycle /ZrO₂ interface is still not good enough. Consequently, we raise Al₂O₃ to 5 cycles for improving the properties. From **Fig. 2.13 (a) (b)**, we can't observe the difference between the as-deposited one and the PDA 300 °C one by the naked eye. But from **Table 2.2** and **Table 2.3**, we still find PDA 300 °C is slightly better than the as-deposited one. And From **Fig. 2.13 (b) (c) (d)**, although the capacitance value at Vg = -2 volts with PDA 500 °C is the largest, the frequency dispersion and the hysteresis of all the samples with PDA 300 °C still display the best. This indicates that the samples through appropriate annealing process might be getting better. After that, from **Fig. 2.14 (a) (b) (c) (d)**, the conductance maps from negative to positive gate voltage and from high to low frequency, the variation of contours are more conspicuous especially at PDA 500 °C, which reveal the interface states may mix up with minority carrier response and getting worse. Particularly, there is a distinct variation at low frequency with high negative gate voltage from **Fig. 2.14 (c) (d)**, which might show the border trap response of high-k dielectrics.

Furthermore, from **Fig. 2.15** (a) (b), the accumulation, depletion, and inversion region of the MOSCAPs of the as-deposited one and PDA 300 °C one are the same in substance. The

frequency dispersion and hysteresis are demonstrated that the as-deposited one ($\Delta C=25.0\%$, $\Delta V=0.31 V$) is slightly worse than PDA 300 °C ($\Delta C=24.4\%$, $\Delta V=0.29 V$), are shown in **Table 2.2** and **Table 2.3**. Then from **Fig. 2.15 (b) (c) (d)**, even if we see the capacitance at accumulation region get larger as increasing PDA temperature, the electrical characteristics are still worse. This might be the oxide trap capacitance induced and interact with the accumulation capacitance. Moreover, the conductance maps at low frequency around 0V to high V_g of all the samples show that PDA 500 °C has a high distribution of interface traps response, and the position of Fermi-level pinning is moved from 10 kHz to around 100 kHz by the location of the concentric circles, are shown in **Fig. 2.16 (a) (b) (c) (d)**. Besides, we conjecture the energy loss signal around V_g= 2 volts is mainly due to gate leakage.

2.4.2 Comparison of Various Al₂O₃ cycles as Inter-layer of ALD-TMA/ZrO₂ on Electreical Characteristics

From Fig. 2.17 to Fig. 2.20, we notice that the higher Al_2O_3 cycles inserting in ALD-TMA/ZrO₂ is, the optimum capacitor performance is. These results indicate that the more Al_2O_3 inter-layer is effective to passivate the substrate surface and significantly to reduce frequency dispersion and hysteresis at the $ZrO_2/In_{0.53}Ga_{0.47}As$ interfaces. In addition, we already know that incorporating several cycles of Al_2O_3 can improve the oxide and interface quality from *C-V* and *G-V* characteristics, which is demonstrated experimentally with aforementioned section, but still not realize the quantitative density of interface trap states. In next section, we will introduce conductance method to extract D_{it} and compare the different conditions.
2.5 Conductance Method

Impedance measurements of MOSCAPs as a function of voltage, frequency, and temperature of high-k/semiconductor interfaces contain contributions from D_{it} that can be extracted in different ways [36]. The conductance method, established by Nicollian and Goetzberger in 1967, is one of the sensitive methods to quantify D_{it} [37]. It is the most complete method, because it yields D_{it} in the depletion and weak inversion portion of the band gap and the capture cross-sections for majority carriers. Although Berglund, Terman and high-low frequency extracted methods could determine interface states, they might overestimate the D_{it} value on low band gap III-V semiconductor because the signal may induce by minority carrier response. Fig 2.21 (a) shows energy band diagram of *n*-type MOSCAP in depletion region. A dc gate bias is applies to the gate which superimpose on a small amplitude (~25 mV) ac signal with frequency f (typically between 1 MHz and 100 Hz). Besides, it displays an arbitrary interface states density distribution, the Fermi level E_F and the intrinsic level E_I. The gate voltage V_g which determines the Fermi level position at the interface induces a space charge and band bending. The ac signal causes a periodic change in band bending and the gate bias determines the energy level position where the Fermi level oscillates at the interface. The traps with energy levels near the Fermi level are capable of changing their occupancy. The conductance is representing the loss mechanism due to interface trap capture and emission of carriers. The equivalent circuit of MOSCAP with interface states in depletion region appropriate for the conductance method is simplified as shown in Fig. 2.21 (b). It consists of the gate oxide capacitance, C_{ox} , the semiconductor capacitance, C_{dos} (ω, ψ_s), the interface trap capacitance, C_{it} (ω, ψ_s), equivalent parallel conductance, $G_p(\omega, \psi_s)$ and a series resistance, R_s . The simplified circuit model supposes the minority carrier response is negligible. The equivalent circuit of impedance analyzer with the measured capacitance C_m and conductance G_m is shown in **Fig. 2.21** (c). The frequency dependence is related with the characteristic trap response time, $\tau = 2\pi/\omega$, where ω is the angular frequency (f is measured frequency).

The interface trap capacitance which is induced by the interface state density is

 $C_{it} = qD_{it}$, where q is the elemental charge. The trap response time for hole is given by Shockley-Read-Hall statistics of capture and emission rate:

$$\tau_h = \left(\sigma \upsilon_{th,h} N_{\nu}\right)^{-1} \exp\left[\frac{E_t - E_{\nu}}{k_B T}\right]$$
(2.2)

where E_t is the trap energy level in the band gap, σ is the capture cross section, $v_{th,h}$ is the average thermal velocity of majority carriers (hole), N_v is the effective DOS of the majority carrier (hole) band, k_B is the Boltzmann constant, and *T* is the temperature.

The conductance method is the way of analyzing the loss that is caused by the variation in the trap level charge state. In fact, interface trap are continuously distributed all over the band gap rather than single energy level. Capture and emission occurs chiefly by traps located within a few kT/q above and below the Fermi level, giving rise to a time constant dispersion and indicating the normalized conductance as follows:

$$\frac{G_p}{\omega} = \frac{qD_{it}}{2\omega\tau_{it}}\ln\left[1 + (\omega\tau_{it})^2\right]$$
(2.3)

The circuit from **Fig. 2.21** (b) to (c) gives G_P/ω in terms of the oxide capacitance C_{ox} , the measured capacitance C_m , and the measured conductance G_m , are shown as follows:

$$\frac{G_p}{\omega} = \frac{\omega G_m C_{ox}^2}{G_m^2 + \omega^2 (C_{ox} - C_m)^2}$$
(2.4)

An approximate expression given the interface trap density in terms of the measured maximum conductance is:

$$D_{it} \approx \frac{2.5}{Aq} \left(\frac{G_p}{\omega}\right)_{\max} \text{ as } \omega \tau_{it} \approx 2$$
(2.5)

where A is the device area. In addition, E_t can be determined at the specific frequency from $(G_p/\omega)_{max}$ and applying Eq. (2.2). Fig. 2.22 shows the behavior of the interface trap time constant at room temperature as a function of capture cross section, which determines the part of interface traps in the band gap observable in the MOS admittance characteristic. Fig. 2.23 shows trap level position calculated from Eq. (2.2) using the values for the average thermal velocity and the density of state band for $In_{0.53}Ga_{0.47}As$ and a capture cross section $\sigma = 1 \times 10^{-17}$ cm², which chosen from Fig. 2.22. The trap characteristic frequency as a function of temperature determines the part of interface traps in the band gap conspicuously in the MOS admittance characteristic. Because of the representative measurement frequency between 100 Hz and 1 MHz, it's difficult to extract the interface state density over the whole band gap at room temperature. Nevertheless, the D_{it} of whole band gap profiles can be extracted by measuring in the various temperatures. For In_{0.53}Ga_{0.47}As, the traps near midgap could be observed at room temperatures. However, if we want to determine the traps which close to the band edges, we have to measure the impedance at lower temperature because of the increasing of the trap response time. Next section, we extract D_{it} at room temperature and compare the influence of the interface state with various PDA conditions in same Al₂O₃ inter-layer and various Al₂O₃ cycles at same PDA conditions. As well correspond to XPS interfacial chemical properties. 11

2.5.1 MOSCAPs with FGA under Various PDA Conditions

Fig 2.24 (a) (b) (c) (d) show parallel conductance maps of *p*-type Pt/Ti/TMA+Al₂O₃ 1cycle+ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs with FGA under different PDA conditions, at temperature 300K. The D_{it} is estimated by the multiple peak values of the curves, which indicate the maximum of $[(G_p/\omega)/Aq]$ with a factor of 2.5[see **Eq. 2.5**]. In **Fig 2.24**, all maps show distinct signal at the gate voltage between -1 and -2 volts and lower frequency. We speculate that these responses might be the bulk oxide traps or slow traps, resulting in high frequency dispersion at V_g = -2 volts, which is consistent with aforementioned section. Among these plots, we can find the color variation in this region is more indistinct with PDA 300 °C. However, because of a great deal of slow traps signal at accumulation region, the response of D_{it} at depletion region is suppressed and results in more invisible signal. Therefore, the $[(G_p/\omega)/Aq]$ -*f* curves from **Fig. 2.25** are demonstrated here, and the interface states can be acquired with the factor of 2.5. From these curves, we can find that the peak value is getting larger as increasing PDA temperature. From **Fig. 2.30** (a) and **Table 2.4**, it is observed that the D_{it} of PDA 300 °C is slightly smaller than the as-deposited one, but mostly better than PDA 400 °C and 500 °C. Accordingly, higher PDA temperature should be avoided so as to prevent the inferior native oxide and interface quality which might degrade electrical characteristics.

Furthermore, the parallel conductance maps of $Al_2O_3 5$ cycles inter-layer are shown in **Fig. 2.26** and the $[(G_p/\omega)/Aq]$ curves in **Fig. 2.27** with FGA under various PDA condition. These contour maps also show the slow traps at the high negative gate voltage, especially at PDA 500 °C. Because of the signal between V_g = -1 and -2 volts at lower frequency is much stronger than the response of interface states, we can't see more obviously about the D_{it} signal. Then, we define the interface state quantitatively by **Fig. 2.27** and show in **Fig. 2.30** (b) and **Table 2.4**. Compare to these values with various PDA temperatures, we demonstrate that the D_{it} at PDA 300 °C is much lower than others.

Moreover, from **Fig. 2.28** and **Fig. 2.29**, for Al_2O_3 10cycles inter-layer, the signal of PDA 500 °C in accumulation region is apparent and the peak of the $[(G_p/\omega)/Aq]$ curves is more seriously. Then, from **Fig. 2.30** (c) and **Table 2.4**, these values indicate that the PDA 300 °C one is the best case of all the samples.

In order to be convinced of the conclusion which the PDA 300 °C is the best one of all the conditions and to prevent more Al_2O_3 inter-layer from interfering with the signal between ALD-TMA/Al₂O₃ and Al₂O₃/ZrO₂ interface, we analyze the interfacial chemistry characteristics of ALD-TMA/Al₂O₃ 1 cycle/ZrO₂ on p-type $In_{0.53}Ga_{0.47}As$ with FGA under different PDA conditions.

XPS spectra were taken by Ga $2p_{3/2}$, In $3d_{5/2}$, and As $2p_{3/2}$ core levels in Fig. 2.35 (a) (b), and (c). Deconvolution of XPS lines involves Shirley baseline removal and Lorentzian-Gaussian doublets as fitting components [38-40]. From Fig. 2.35 (a), there is no significant variation in Ga $2p_{3/2}$ spectra. Nevertheless, the In $3d_{5/2}$ and As $2p_{3/2}$ spectra show the presence of In- and As-oxide in both samples, are shown in Fig. 2.35 (b) (c). Upon different annealing temperatures, it is possible that there are some oxygen bonds transfer processes from one oxidation to another. In other words, the As⁵⁺ oxidation state is seen to undergo an oxygen transfer to the As^{3+} with the small As^{2+} state related component after specific annealing conditions. The As₂O₅ portion of the native oxide decreases with the As₂O₃ increases; this suggests that the arsenic oxides undergo a bond conversion from one form of arsenic oxide to another. However, the In³⁺ and the InAsO₄ oxides are seen to increase, whereas there is an unobvious signal in the gallium oxide states suggesting this signal takes place as a result of oxygen bond transfers from gallium to indium. The Table 2.5 shows the ratio of the fitted area such as In_2O_3 to $InAsO_4$ from In $3d_{5/2}$ spectra, As^{2+} to As_2O_5 and As_2O_3 to As₂O₅ from As $2p_{3/2}$ spectra. With evidence in Fig. 2.37 (a), these area ratio were compared to the electrical characteristics, we can illustrate that the better interface property is caused by the higher ratio values of the superior oxide. This phenomenon may be caused by the passivation of the trivalent oxides or lower valence As on the interface. Therefore, we can demonstrate that the PDA 300 °C is the best condition in our samples.

2.5.2 Comparison of Various Al₂O₃ cycles with same PDA Conditions

Fig. 2.31 shows the comparison of D_{it} profiles of ALD-TMA/ZrO₂/In_{0.53}Ga_{0.47}As

MOSCAPs with various Al₂O₃ inter-layers at the same PDA conditions, which are measured at 300K. These diagrams show that incorporating more Al₂O₃ inter-layers with ALD-TMA/ZrO₂, the oxide and interface quality will be more improvable, especially at PDA 300 °C. It indicates that the interface could be passivated within Al₂O₃. Therefore, we further compare the electrical properties of ALD-TMA/ZrO₂ case which means Al₂O₃ 0cycle inter-layer [see **Fig. 2.32**] and the ALD-TMA/Al₂O₃ case which means all of the gate dielectric is composed of Al₂O₃ [see **Fig. 2.33**] with Al₂O₃ 1,5, and 10 cycles inter-layer under PDA 300 °C/120s, w/FGA. From **Fig. 2.34** and **Table 2.4**, we notice that thicker Al₂O₃ might passivate the In_{0.53}Ga_{0.47}As surface, the oxide and interface quality might be improved [41]. In addition, we will analyze the interfacial chemistry characteristics of ALD-TMA/ZrO₂ with various Al₂O₃ inter-layers under PDA 300 °C to prove the aforementioned results.

The Ga $2p_{3/2}$, In $3d_{5/2}$, and As $2p_{3/2}$ core levels of XPS spectra are reported in **Fig. 2.36** (a) (b), and (c) for ALD-TMA/Al₂O₃ 0, 1, 5, 10cycle/ZrO₂ 10cycle on p-type In_{0.53}Ga_{0.47}As, respectively, except the top one. It is found that the signal of Ga $2p_{3/2}$ spectra hardly depends on the various Al₂O₃ inter-layer. However, we can notice the variation at the In $3d_{5/2}$ and As $2p_{3/2}$ spectra. When increasing Al₂O₃ inter-layers, the As₂O₅ decreases with the As₂O₃ and As²⁺ increase. It indicates that the more Al₂O₃ layer tend to displace the As⁵⁺ oxidation state to the As³⁺ and As²⁺. From **Table 2.6**, we can see that the area ratio of In₂O₃ to InAsO₄, As²⁺ to As₂O₅, and As₂O₃ to As₂O₅ increase when inserting Al₂O₃ 10cycles between the ZrO₂ and the In_{0.53}Ga_{0.47}As interface. To further demonstrate the connection between electrical and chemical characteristics of the interface, we combine the density of interface state with the area ratio in the profile. From **Fig. 2.37** (b), it shows that the interface can be effectively passivated by trivalent oxides such as Al₂O₃ and As₂O₃ without generating a large amount of dangling bonds [42]. Consequently, we show that the Al₂O₃ 10cycles inter-layer condition is better than other conditions.

2.6 Summary

In the past, poor gate dielectric quality and interface among oxide/semiconductor could results in frequency dispersion, hysteresis, and inferior interface property. Therefore, first of all, we demonstrate the TMA precursor of ALD can achieve more self-cleaning capability than TEMAZ at the oxide/In_{0.53}Ga_{0.47}As interface. Furthermore, various Al₂O₃ inter-layers with FGA under different PDA conditions have been conferred. According to the electrical characteristics of frequency dispersion and hysteresis, the capacitor under PDA 300 °C with FGA displays the better property than other temperatures. This result indicates that proper temperature of PDA is important due to the higher temperature might produce inferior native oxide like As₂O₅ or InAsO₄ from XPS analysis which gives rise to higher D_{it} existed in midgap from the extraction of the conductance method. In addition, more Al₂O₃ cycles inserting among ALD-TMA/ZrO₂ show the optimum electrical performance. It is observed that the interface of ZrO₂/In_{0.53}Ga_{0.47}As is effectively passivated by trivalent oxides such as Al₂O₃ and As₂O₃ without generating a large amount of dangling bonds and demonstrate that -100 the interface have better quality.

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Fig. 2.1 Capacitive equivalent thickness (CET) vs. physical thickness as measured in a MOSCAPs for various ALD dielectrics on $In_{0.53}Ga_{0.47}As$.

Gate dielectric(ALD)	$\Delta \mathbf{E}_{\mathbf{v}}\left(\mathbf{eV} ight)$	$\Delta E_{c} (eV)$	E _g (eV)
ZrO ₂	2.63±0.1	2.13±0.3	5.5±0.2
HfO ₂	3.04±0.1	1.8±0.3	5.6±0.2
Al ₂ O ₃	4.09±0.1	2.8±0.3	7.65±0.2

Table 2.1 Band offsets of various dielectrics with respect to $In_{0.53}Ga_{0.47}As$ as measured bysynchrotron radiation photoelectron spectroscopy.

- Surface pretreatment
 - Acetone (5min)
 - Isopropanol (5min)
 - $HCl: H_2O = 1:10$ (2min)
- \blacktriangleright Deposited by ALD at 250 °C
 - TEMAZ or TMA 10cycles pretreatment
 - ZrO₂ 80 cycles.
- Annealing condition
 - PDA (300.400.500°C/120s)
- Gate electrode patterning and formation(Ti/Pt)
- Backside-contact deposition (Ti/Pt)
- > FGA 10% H_2 +90% N_2 (250°C/30min.)

Fig. 2.2 Process flow of MOSCAPs with different surface pretreatments.

Ti/Pt

100

TEMAZ or **TMA/ZrO₂**

p-In_{0.53}Ga_{0.47}As (100) channel layer

 $p-In_{0.53}Ga_{0.47}As$ (100) buffer layer

p-InP (100)

Ti/Pt

Fig. 2.3 MOSCAPs structure with ALD-TEMAZ or $TMA/ZrO_2/In_{0.53}Ga_{0.47}As$.

- Surface pretreatment
 - Acetone (5min)
 - Isopropanol (5min)
 - $HCl: H_2O = 1:10$ (2min)
- \blacktriangleright Deposited by ALD at 250 °C
 - TMA 10cycles
 - Al₂O₃ 1.5.10 cycles
 - ZrO₂80 cycles.
- Annealing condition
 - as-deposited or PDA (300.400.500 °C/120s)
- Gate electrode patterning and formation(Ti/Pt)
- Backside-contact deposition (Ti/Pt)
- > FGA 10% H_2 +90% N_2 (250°C/30min.)

Fig. 2.4 Process flow of the MOSCAPs with several cycles of Al₂O₃.

Ti/Pt

100

ZrO₂ TMA/Al₂O₃ 1.5.10cycles

 $p-In_{0.53}Ga_{0.47}As$ (100) channel layer

p-In_{0.53}Ga_{0.47}As (100) buffer layer

p-InP (100)

Ti/Pt

Fig. 2.5 MOSCAPs structure with ALD-TMA/Al₂O₃/ZrO₂/In_{0.53}Ga_{0.47}As.



Fig. 2.6 TEM image of the as-deposited ALD-TMA/Al₂O₃ 10 cycle/ZrO₂ on In_{0.53}Ga_{0.47}As





Fig. 2.7 Multi-frequency C-V curves for p-type Pt/Ti/TEMAZr+ZrO₂/In₀.53Ga₀.47As MOSCAPs measured from 1 MHz to 100 Hz after FGA under different PDA conditions in N₂ ambience for 120 s (a) 300 °C (b) 400 °C (c) 500 °C



Fig. 2.8 Map of normalized conductance $G/A\omega q$ (eV⁻¹cm⁻²) vs. V_g (volt) for *p*-type Pt/Ti/TEMAZr+ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs measured from 1 MHz to 100 Hz after FGA under different PDA conditions in N₂ ambience for 120 s (a) 300 °C (b) 400 °C (c) 500 °C



Fig. 2.9 Multi-frequency *C-V* curves for *p*-type Pt/Ti/TMA+ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs measured from 1 MHz to 100 Hz after FGA under different PDA conditions in N₂ ambience for 120 s (a) 300 °C (b) 400 °C (c) 500 °C.



Fig. 2.10 Map of normalized conductance G/Aωq (eV⁻¹cm⁻²) vs. V_g (volt) for *p*-type Pt/Ti/TMA+ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs measured from 1 MHz to 100 Hz after FGA under different PDA conditions in N₂ ambience for 120 s (a) 300 °C (b) 400 °C (c) 500 °C



Fig. 2.11 Multi-frequency C-V curves for p-type Pt/Ti/TMA+Al₂O₃ 1 cycle+ZrO₂/In_{0.53}Ga_{0.47}. As MOSCAPs measured from 1 MHz to 100 Hz after FGA under different PDA conditions in N₂ ambience for 120 s (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.



Fig. 2.12 Map of normalized conductance $G/A\omega q$ (eV⁻¹cm⁻²) vs. V_g (volt) for *p*-type Pt/Ti/TMA+Al₂O₃ 1 cycle+ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs measured from 1 MHz to 100 Hz after FGA under different PDA conditions in N₂ ambience for 120 s (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.



Fig. 2.13 Multi-frequency C-V curves for p-type Pt/Ti/TMA+Al₂O₃ 5 cycle+ZrO₂/In_{0.53}Ga_{0.47}. As MOSCAPs measured from 1 MHz to 100 Hz after FGA under different PDA conditions in N₂ ambience for 120 s (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.



Fig. 2.14 Map of normalized conductance $G/A\omega q$ (eV⁻¹cm⁻²) vs. V_g (volt) for *p*-type Pt/Ti/TMA+Al₂O₃ 5 cycle+ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs measured from 1 MHz to 100 Hz after FGA under different PDA conditions in N₂ ambience for 120 s (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.



Fig. 2.15 Multi-frequency C-V curves for p-type Pt/Ti/TMA+Al₂O₃ 10 cycle+ZrO₂/In_{0.53}Ga-_{0.47}As MOSCAPs measured from 1 MHz to 100 Hz after FGA under different PDA conditions in N₂ ambience for 120 s (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.



Fig. 2.16 Map of normalized conductance G/Aωq (eV⁻¹cm⁻²) vs. V_g (volt) for *p*-type Pt/Ti/TMA+Al₂O₃ 10 cycle+ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs measured from 1 MHz to 100 Hz after FGA under different PDA conditions in N₂ ambience for 120 s (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.



Fig. 2.17 Multi-frequency C-V curves for various Al₂O₃ cycles measured from 1 MHz to 100 Hz after FGA under as-deposited (a) Al₂O₃ 1 cycle (b) Al₂O₃ 5 cycle (c) Al₂O₃ 10 cycle.



Fig. 2.18 Multi-frequency *C-V* curves for various Al₂O₃ cycles measured from 1 MHz to 100 Hz after FGA under PDA 300 °C /120 s (a) TMA pretreatment (Al₂O₃ 0 cycle) (b) Al₂O₃ 1 cycle (c) Al₂O₃ 5 cycle (d) Al₂O₃ 10 cycle.



Fig. 2.19 Multi-frequency C-V curves for various Al₂O₃ cycles measured from 1 MHz to 100 Hz after FGA under PDA 400 °C /120 s (a) TMA pretreatment (Al₂O₃ 0 cycle) (b) Al₂O₃ 1 cycle (c) Al₂O₃ 5 cycle (d) Al₂O₃ 10 cycle.



Fig. 2.20 Multi-frequency C-V curves for various Al₂O₃ cycles measured from 1 MHz to 100 Hz after FGA under PDA 500 °C /120 s (a) TMA pretreatment(Al₂O₃ 0 cycle) (b) Al₂O₃ 1cycle (c) Al₂O₃ 5 cycle (d) Al₂O₃ 10 cycle.

$\triangle C (@V_g = -2 V)$ (w/FGA)	as-deposited	PDA 300 °C /120 s	PDA 400 °C /120 s	PDA 500 °C /120 s
TEMAZ		99.4%	160.9%	129.5%
TMA		42.7%	84.3%	75.9%
Al ₂ O ₃ 1cyc.	43.4%	41.7%	79.4%	55.7%
Al ₂ O ₃ 5cyc.	40.9%	37.8%	65.3%	46.7%
Al ₂ O ₃ 10cyc.	25.0%	24.4%	34.8%	33.6%

Table 2.2 Overview of frequency dispersion ΔC of various pretreatments and several Al₂O₃



Hysteresis (V) (w/FGA)	as-deposited	PDA 300 °C /120 s	PDA 400 °C /120 s	PDA 500 °C /120 s
TEMAZ		0.96	0.76	0.61
TMA		0.59	0.74	0.66
Al ₂ O ₃ 1cyc.	0.49	0.44	0.70	0.54
Al ₂ O ₃ 5cyc.	0.48	0.43	0.62	0.46
Al ₂ O ₃ 10cyc.	0.31	0.29	0.43	0.37

Table 2.3 Overview of hysteresis (V) of various pretreatments and several Al₂O₃ cycles with FGA under various PDA conditions.



Fig. 2.21 Energy band diagram of a *n*-type MOSCAPs in depletion region is shown in (a). A dc gate bias V_g with a small ac signal of frequency *f* are applied, causing a band bending ψ_s in the semiconductor and interface trap response with time constant τ.
(b) Equivalent circuit of MOSCAPs in depletion region. (c) Measured capacitance C_m and conductance G_m.



Fig. 2.22 Behavior of the interface trap time constant at room temperature as a function of capture cross section determines the part of interface traps in the band gap observable in the MOS admittance characteristics. 10⁹ Characteristic Frequency (Hz) e - \mathbf{h}^{+} 300K 250K **10**³ 200K 150K 100K 77K 10^{1} [0.0 0.2 0.4 0.6 Energy in Bandgap (eV)

Fig. 2.23 The trapped charge characteristics for $In_{0.53}Ga_{0.47}As$ under different temperature and corresponding measurement window from 1 MHz to 100 Hz *C-V* measurement frequency.



Fig. 2.24 Map of normalized parallel conductance, (G_p/ω)/Aq (eV⁻¹cm⁻²) vs. V_g (volt) for p-type Pt/Ti/TMA+Al₂O₃ 1 cycle+ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs measured from 1 MHz to 100 Hz after FGA under different PDA conditions in N₂ ambience for 120 s (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.



Fig. 2.25 Parallel conductance curves of for *p*-type Pt/Ti/TMA+Al₂O₃ 1 cycle+ZrO₂/In_{0.53}Ga-_{0.47}As MOSCAPs after FGA under different PDA conditions from V_g = -0.35 to +0.1 volts (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.


Fig. 2.26 Map of normalized parallel conductance, (G_p/ω)/Aq (eV⁻¹cm⁻²) vs. V_g (volt) for p-type Pt/Ti/TMA+Al₂O₃ 5 cycle+ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs measured from 1 MHz to 100 Hz after FGA under different PDA conditions in N₂ ambience for 120 s (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.



Fig. 2.27 Parallel conductance curves of for *p*-type Pt/Ti/TMA+Al₂O₃ 5 cycle+ZrO₂/In_{0.53}Ga-_{0.47}As MOSCAPs after FGA under different PDA conditions from V_g = -0.5 to +0.2 volts (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.



Fig. 2.28 Map of normalized parallel conductance, (G_p/ω)/Aq (eV⁻¹cm⁻²) vs. V_g (volt) for p-type Pt/Ti/TMA+Al₂O₃ 10 cycle+ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs measured from 1 MHz to 100 Hz after FGA under different PDA conditions in N₂ ambience for 120 s (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.



Fig. 2.29 Parallel conductance curves of for *p*-type Pt/Ti/TMA+Al₂O₃ 10 cycle+ZrO₂/In_{0.53}. Ga_{0.47}As MOSCAPs after FGA under different PDA conditions from V_g = -0.7 to +0.1 volts (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.



Fig. 2.30 Comparison of D_{it} profiles of ALD-TMA/ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs under different PDA conditions with various Al₂O₃ inter-layer (a) 1cycle (b) 5cycle (c) 10cycle.



Fig. 2.31 Comparison of D_{it} profiles of ALD-TMA/ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs with various Al₂O₃ inter-layers under different PDA conditions (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.



(b)

Fig. 2.32(a)(b) The map of normalized parallel conductance, $(G_p/\omega)/Aq$ (eV⁻¹cm⁻²) vs. V_g (volt) and the curves for *p*-type Pt/Ti/TMA+ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs from V_g= -0.25 to +0.1 volts under PDA 300 °C/120 s, w/FGA



Fig. 2.33 (a)(b)(c) The capacitance curve, the map of normalized parallel conductance, and $(G_p/\omega)/Aq \ (eV^{-1}cm^{-2}) \ vs. \ V_g \ (volt) \ and \ the \ [(G_p/\omega)/Aq] \ curves \ for \ p-type$ $Pt/Ti/TMA+Al_2O_3/In_{0.53}Ga_{0.47}As \ MOSCAPs \ from \ V_g= -0.05 \ to \ +0.6$ volts under PDA 300 °C/120 s, w/FGA



Fig. 2.34 Comparison of D_{it} profiles of In_{0.53}Ga_{0.47}As MOSCAPs with various Al₂O₃ cycle inter-layer and ALD-Al₂O₃/In_{0.53}Ga_{0.47}As MOSCAPs under PDA 300 °C/120 s, w/FGA.

D _{it} (10 ¹² eV ⁻¹ cm ⁻²)	Осус	1cyc	5cyc	10cyc	Al ₂ O ₃
As-deposited+FGA		9.26	8.70	5.40	
PDA 300°C+FGA	9.37	8.57	7.83	4.99	3.75
PDA 400°C+FGA		16.87	14.0	7.71	
PDA 500°C+FGA		17.21	16.49	14.71	

Table 2.4 Overview of D_{it} at trap energy $E_t = 0.377 \text{eV}$ of ALD-TMA/ZrO₂/In_{0.53}Ga_{0.47}As underdifferent thermal conditions and Al₂O₃/In_{0.53}Ga_{0.47}As MOSCAPs at PDA 300°C/120 s, w/FGA.







Fig. 2.35 X-ray photoelectron spectroscopy for *p*-type Pt/Ti/TMA+Al₂O₃ 1 cycle+ZrO₂/In_{0.53}.

Ga_{0.47}As MOSCAPs after FGA under various PDA conditions (a) Ga $2p_{3/2}$ (b) In

 $3d_{5/2}$ (c) As $2p_{3/2}$.

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PDA 300 °C/120s,w/FGA



Fig. 2.36 X-ray photoelectron spectroscopy of various pretreatment and several Al₂O₃ cycles

after FGA under PDA 300 °C /120 s (a) Ga $2p_{3/2}$ (b) In $3d_{5/2}$ (c) As $2p_{3/2}$

Al ₂ O ₃ 1cycle	As^{2+}/As_2O_5	As ₂ O ₃ /As ₂ O ₅	In ₂ O ₃ /InAsO4
As-deposited+FGA	0.393	1.145	0.458
PDA 300 °C /120 s+FGA	0.417	1.156	0.488
PDA 400 °C /120 s+FGA	0.225	0.910	0.283
PDA 500 °C /120 s+FGA	0.219	0.902	0.274

Table 2.5 Ratio of the fitted area from the As $2p_{3/2}$ and In $3d_{5/2}$ spectra for *p*-typePt/Ti/TMA+Al_2O_3 1 cycle+ZrO_2/In_{0.53}Ga_{0.47}As MOSCAPs after FGA under
various PDA conditions.

PDA 300 °C/120 s w/FGA	As ²⁺ /As ₂ O ₅	As ₂ O ₃ /As ₂ O ₅	In ₂ O ₃ /InAsO4
TEMAZ	0.210	0.867	0.228
TMA	0.225	0.916	0.364
Al ₂ O ₃ 1cyc.	0.417	1.156	0.488
Al ₂ O ₃ 5cyc.	0.915	1.543	0.501
Al ₂ O ₃ 10cyc.	1.068	1.624	0.703

Table 2.6 Ratio of the fitted area from the As $2p_{3/2}$ and In $3d_{5/2}$ spectra at various pretreatment and several Al₂O₃ cycles after FGA under PDA 300 °C/120 s.



Fig. 2.37 Comparison of D_{it} and ratio of the fitted area from the As 2p_{3/2} and In 3d_{5/2} spectra profiles of ALD-TMA/ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs (a) with Al₂O₃ 1 cycle inter-layer (b) with PDA 300 °C /120 s, w/FGA.

Chapter 3

The Extraction of Border Traps for ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs by a Distributed Bulk-Oxide Traps Model

3.1 Introduction

The concept of border traps has been introduced by Dan Fleetwood in 1992 [1] to define traps in the gate dielectrics of high-k/III-V MOS devices, which result in frequency dispersion at the accumulation region. The traps have been attributed to trapped-holes [2] or to oxygen deficiency defects [3]. As a rule, the density of border traps increases when the quality of the oxide decreases, due to poor stoichiometry or the presence of strained bonds at the interface [4]. However, the conventional interface states whose time constant in such bias regions is far shorter than the period of typical measurement frequencies can't be used to explain this dispersion phenomenon. On the other hand, the trap states reside the high- κ dielectric, which are called border traps or slow oxide traps, have long time constants when thay exchange charge with the channel [5]. Furthermore, the frequency dispersion of conductance doesn't follow the renowned peak deportment when the conventional conductance method [6] for the interface states is applied to the high to low transition (the maximum slope) of the C-V data. In addition, comparing the experimental C-V curve with the ideal case demonstrates that the density of interface state far surpass which is extracted from the dispersion in that region. Such variance can be resolved by a border trap model in which the low frequency portion give rise to the stretch-out C-V curve is stronger than the high-frequency portion for the dispersion.

In this chapter, the distributed border traps model is completed by adding integration of

the trap density with respect to energy for calculating the equivalent admittance. A differential equation is derived and numerically solved to produce frequency-dependent capacitance and conductance of the MOS devices. The model is validated and calibrated by the experimental data of p-type ALD- ZrO_2 / Al_2O_3 / $In_{0.53}Ga_{0.47}As$ MOSCAPs in accumulation region.

3.2 A Distributed Model for determining Border Traps

In general, the bulk oxide traps can interchange charge with mobile carriers in the semiconductor bands by tunneling mechanism in devices. Hence, **Fig. 3.1** schematically exhibits the mechanism between bulk-oxide traps and valence band of the p-type MOS devices in the accumulation gate bias. The time constant connected with charge exchange between bulk-oxide traps and semiconductor is regulated by tunneling mechanism that has exponential dependence on the trap distance x from the interface of oxide/semiconductor [5, 7-10] as follows:

$$\tau(x) = (1 - f_0)\tau_0 e^{2\kappa x}$$

(3.1)

Here, τ_0 is the time constant of the interface trap which equals $1/(n_s \sigma v_{th})$ with σ being the trap cross-sectional area, and v_{th} is the thermal velocity of hole. Other parameters in Eq.(3.1) are as follows: f_0 is the Fermi-Dirac function which a trap occupied by an electron at energy E, and κ is the attenuation coefficient for an energy E wavefunction of an hole decaying due to an energy barrier $E_{v,ox} > E$.

$$\kappa = \sqrt{2m^*(E_{\nu,ox} - E)}/\hbar \tag{3.2}$$

 m^* is the hole effective mass of the gate dielectric, and $E_{v,ox}$ is the bottom energy of the gate insulator band (tunneling barrier), as shown in **Fig. 3.1**.

The bulk-oxide traps at a specific depth x and energy E change occupancy with respond to a small-signal ac modulation for a given dc bias. The border traps at energy about $E \sim E_f$ are most responsible for the small-signal capacitance. In the other words, we assume the border traps located within certain distance from the interface maintain a Fermi level the same as the semiconductor. Then, we can find that the influences of the bulk-oxide traps at certain depth x and energy E can be modeled by a series of connecting capacitance and conductance on the small-signal MOS admittance. The bulk-oxide traps in an incremental depth Δx at x and incremental energy ΔE at E are symbolized by the incremental capacitance $\Delta C_{bt}(E, x)$ and the incremental conductance $\Delta G_{bt}(E, x)$ which are connected in series. If the density per volume per energy of bulk-oxide traps is N_{bt} in units of eV⁻¹cm⁻³, then [5-6] the equation of ΔC_{bt} will indicates:

$$\Delta C_{\rm bt}(E,x) = \frac{f_0(1-f_0)q^2 N_{\rm bt}}{kT} \Delta E \,\Delta x \tag{3.3}$$

And the $\Delta C_{\rm bt}(E, x)$ and $\Delta G_{\rm bt}(E, x)$ have the relationship in time constant $\tau(x)$

$$\frac{\Delta C_{bt}(E,x)}{\Delta G_{bt}(E,x)} = \tau(x) = (1 - f_0)\tau_0 e^{2\kappa x}$$
(3.4)

In order to integrate with the continuous energy distribution of bulk-oxide traps, the $\Delta C_{bt}(E, x)$ and $\Delta G_{bt}(E, x)$ in serial combination have to be transfer to a parallel connection of the incremental admittance $\Delta Y_{bt}(E, x)$. Due to the factor $f_0(1-f_0)$ has pointy peak at $E = E_f$, the attenuation coefficient *k* in **Eq.(3.2**) is determined as a constant with $E = E_f$ in the integration. Therefore, the total incremental admittance at certain depth *x* and energy E is indicated for

$$\Delta Y_{\rm bt}(x) = \int_E \frac{1}{\frac{1}{j\omega\Delta C_{\rm bt}(E,x)} + \frac{1}{\Delta G_{\rm bt}(E,x)}}} = \frac{q^2 N_{\rm bt} \ln(1 + j\omega\tau_0 e^{2\kappa x})}{\tau_0 e^{2\kappa x}} \Delta x$$
(3.5)

Because of a continuous energy distribution of the border trap all over the gate oxide thickness, an equivalent circuit of the distributed model in the MOS device is illustrated in **Fig. 3.2**, where the oxide capacitance is separated into an infinite number of serial slices with branches of $\Delta Y_{bt}(x)$, which is linked in different depth. Here, ϵ_{ox} is the permittivity of the gate dielectric and C_s is the semiconductor capacitance.

Consequently, if we define Y(x) to be the equivalent admittance at the point x looking into the semiconductor in **Fig. 3.2**, the recursive nature of the circuit will give the admittance

of the next point $x + \Delta x$ as

$$Y(x + \Delta x) = \Delta Y_{\text{bt}}(x) + \frac{1}{\frac{\Delta x}{j\omega\epsilon_{ox}} + \frac{1}{Y(x)}}$$
(3.6)

Then, substituting **Eq.(3.5**) for $\Delta Y_{bt}(x)$, the first order terms in Δx will yield a differential equation for Y(x)

$$\frac{dY}{dx} = -\frac{Y^2}{j\omega\epsilon_{ox}} + \frac{q^2 N_{\rm bt} \ln(1+j\omega\tau_0 e^{2\kappa x})}{\tau_0 e^{2\kappa x}}$$
(3.7)

There are two equations as boundary conditions as follows:

$$Y(x=0) = j\omega C_s + j\omega C_{it} + G_{it}$$
(3.8)

where C_s is the semiconductor capacitance and C_{it} and G_{it} are contributions from interface traps and given in [6] as

$$C_{it} = q^2 D_{it} \arctan(\omega \tau_{it}) / (\omega \tau_{it})$$

$$G_{it} = q^2 D_{it} \ln[1 + (\omega \tau_{it})^2] / 2\tau_{it}$$
(3.9)
(3.10)

where D_{it} (eV⁻¹ · cm⁻²) is the interface trap density.

Moreover, Eq.(3.7) need to be numerically solved to obtain the total admittance looked into semiconductor by gate

$$Y(x = t_{ox}) \equiv G_{\text{tot}} + j\omega C_{\text{tot}}$$
(3.11)

For the typical measured frequency limit of 1 kHz - 1 MHz, $1.4*10^{-6} < \omega \tau_0 < 1.4*10^{-3}$, the bulk-oxide traps can't respond to the ac signal and C_{tot} is equal to C_{ox} in series with C_s , so the C_{tot} varies with $\ln(1/\omega)$ linearly, and G_{tot} varies with ω , that is to say, $G_{tot} / \omega \sim \text{constant}$. For a given bias, the constant G_{tot} / ω shows that the response of the border traps causes wide frequency dispersion because of their various depth distribution, in other words, an obvious distinction from conventional interface traps [6]. Then, for a given frequency of $\omega < 1/\tau_0$, the depth of the slow traps that respond to the small-signal can be estimated by making the factor $\omega \tau_0 e^{2\kappa x}$ in **Eq.(3.7)** equal unity, as the exhibition $x \sim (2\kappa)^{-1} \ln(1/\omega\tau_0)$, which is in the range of 0.1~1mm.

When $\omega = 0$ or in dc condition, the circuit of Fig. 3.2 becomes a purely capacitive

circuit model, and Eq.(3.7) is simplified to a real equation for C(x) as follows:

$$\frac{dC}{dx} = -\frac{C^2}{\epsilon_{ox}} + q^2 N_{\rm bt}$$
(3.12)

The capacitance boundary condition at x=0 is C_s . For the uniform distribution of N_{bt} , Eq.(3.12) can be analytically resolved to produce

$$C(x) = C_0 \frac{(C_s + C_0) \exp\left(2qx \sqrt{\frac{N_{\text{bt}}}{\epsilon_{ox}}}\right) + (C_s - C_0)}{(C_s + C_0) \exp\left(2qx \sqrt{\frac{N_{\text{bt}}}{\epsilon_{ox}}}\right) - (C_s - C_0)}$$
(3.13)

Here, $C_0 = q\sqrt{\epsilon_{ox}N_{bt}}$. If $2q\sqrt{\epsilon_{ox}N_{bt}} >> 1$, then $C(x = t_{ox}) \approx \sqrt{q^2 \epsilon_{ox}N_{bt}}$, which is insensitive to C_s . Certainly, this is only a matter of theoretical interest, nevertheless, it would take much longer than the age of the universe to charge up all the border traps in the gate dielectric.

Besides, the C_s in accumulation region of the case is very high. From Eq.(3.13), $C_{tot}(dc) \approx C_0 \text{coth}(C_0/C_{ox})$, is larger than C_{ox} . This result is in contrast to the interface states or lumped-circuit bulk-oxide traps model, which don't yield dispersion when shorted out by large C_s. Consequently, frequency dispersion in accumulation region is a good indicator of distributed bulk-oxide traps. Moreover, the model should be applicable to any oxide/semiconductor interface with border traps since the derivation isn't depend on material. However, some parameters, such as v_{th} and κ , are material dependent and need to be calculated compatibly [11].

Furthermore, the time constant τ_0 is gate-voltage dependent which is assumed to submit standard SRH theory for advanced devices, one should account for inversion layer quantization and its impact on the carrier recombination at the interface. A final factor which must be carefully investigated is that most of the oxide traps show inelastic tunneling transitions, while by default, elastic tunneling is assumed in many cases [4].

3.3 The Relationship between the Model and the measured Multi-frequency *C-V* and *G-V* Electrical property in Accumulation region

To further discuss the effect of bulk-oxide traps in gate dielectrics at accumulation region and extract N_{bt} quantitatively, we have fitted the experimental capacitance and conductance data for the ALD-TMA/ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs under different PDA conditions with several Al₂O₃ layers at the gate voltage range from -2 to -1 volts which are correlated with the distributed model. There are several parameters of the model, such as $N_{\rm bt}$, τ_0 , $C_{\rm s}$, ϵ_{ox} , and k, need to be given an initial supposed values and be matched between the measured data and the oxide traps model from 1 kHz to 100 kHz. Part of the parameters like gate oxide thickness tox is determined by TEM image, the semiconductor capacitance Cs is selected which gives C_{tot} slightly below the capacitance value of 1 MHz at V_g = -2 V. Moreover, due to two kinds of gate dielectric layers in our sample, we have to assign different parameters, such as ϵ_{ox} , k, and t_{ox} for Al₂O₃ and ZrO₂, respectively. Pay more attention to the attenuation coefficient k, we find that Al₂O₃ should be larger than ZrO₂ because of the difference between the valence band of gate oxide and the energy E. And τ_0 is given to probably achieve the frequency condition $\omega \tau_0 \sim 1$, which means the influence of bulk-traps has not existed on the capacitance and conductance characteristics. Finally, we can discover that the consequences of the model and the measured data are matched because of being sensitive to the initial supposed values.

Fig 3.3, 3.5, 3.7, and 3.9 show the transferred *C-V* map of total experimental *C-F* data for the ALD-TMA/ $ZrO_2/In_{0.53}Ga_{0.47}As$ MOSCAPs under different PDA conditions with various Al₂O₃ inter-layers at frequency from 1 kHz to 100 kHz, and Fig 3.4, 3.6, 3.8, and 3.10 display

the converted *G-V* map of total experimental *G-F* data. With these figures of *C-V* and *G-V* maps, the values of N_{bt} are extracted as shown in **Table. 3.1** at $C_s=0.75$ (μ F/cm²), which indicate the surface band bending of semiconductor are in the same conditions. And this substrate capacitance corresponding to the energy E of band gap is above valence band about 0.15 eV.

From **Fig 3.11** and **3.12**, both the slopes of *C*-*F* and *G*-*F* of different PDA conditions are sensitive to bulk-oxide trap density N_{bt} which demonstrate the frequency dispersion at accumulation region, and in contrast with **Table. 3.1**, the temperature of 300 °C has lower N_{bt} in each Al_2O_3 inter-layer conditions except for Al_2O_3 with 1cycle. This might be a slightly error of the extraction. Besides, we compare these results of N_{bt} with the frequency dispersion ΔC in **Table. 2.2**, and have good consistency with the consequence. In addition, the ΔC and N_{bt} of 400 °C and 500 °C have some mismatch; these might be the capacitance values at accumulation region of PDA 500 °C is much higher than 400 °C and result the ΔC at PDA 500 °C in lower values.

Furthermore, from each post-deposition annealing conditions, we demonstrate that the bulk-oxide trap density N_{bt} of thicker Al_2O_3 layers have lower values and low frequency dispersion, as shown in **Fig 3.13**, **3.14**, and **Table 3.1**. This might be the quality of gate dielectric ZrO_2 is not good enough, and the Al_2O_3 inter-layer can be used to improve the oxide and interface characteristics.

3.4 Summary

The distributed bulk-oxide traps model has been developed for the tunneling mechanism which indicate charging and discharging of the border traps between the $In_{0.53}Ga_{0.47}As$ surface and trap states. Besides, due to the broad frequency spectrum of traps response, the model

differs from the usual interface state circuit. However, the model is demonstrated with the measured data in *C-V* and *G-V* curves. And the extraction of density N_{bt} of bulk-oxide traps has similar property which compared to the aforementioned chapter. By this distributed model, we could further demonstrate the consistency with the border traps from the quantitative analyses.



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Fig. 3.2 An equivalent circuit for border traps distributed over the depth x of the gate dielectrics. The semiconductor capacitance is represented by C_s , the interface trap capacitance is C_{it} , and the resistance R_{it} is a lossy process of D_{it} .



Fig. 3.3 The transferred C-V map of total experimental C-F data for p-type $Pt/Ti/TMA+ZrO_2/In_{0.53}Ga_{0.47}As$ MOSCAPs at the frequency 1 kHz ~ 100 kHz from V_g = -1 to -2 volts at PDA (a) 300 °C (b) 400 °C (c) 500 °C ,which compared from the distributed border trap model.



Fig. 3.4 The transferred G-V map of total experimental G-F data for p-type $Pt/Ti/TMA+ZrO_2/In_{0.53}Ga_{0.47}As$ MOSCAPs at the frequency 1 kHz ~ 100 kHz from V_g = -1 to -2 volts at PDA (a) 300 °C (b) 400 °C (c) 500 °C ,which compared from the distributed border trap model.



Fig. 3.5 The transferred *C-V* map of total experimental *C-F* data for *p*-type Pt/Ti/TMA+Al₂O₃ 1 cycle+ZrO₂/In_{0.53}Ga_{0.47}As at the frequency 1 kHz ~ 100 kHz from V_g= -1 to -2 volts at (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C ,which compared from the distributed border trap model.



Fig. 3.6 The transferred *G-V* map of total experimental *G-F* data for *p*-type Pt/Ti/TMA+Al₂O₃ 1 cycle+ZrO₂/In_{0.53}Ga_{0.47}As at the frequency 1 kHz ~ 100 kHz from V_g = -1 to -2 volts at (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C ,which compared from the distributed border trap model.



Fig. 3.7 The transferred *C-V* map of total experimental *C-F* data for *p*-type Pt/Ti/TMA+Al₂O₃ 5 cycle+ZrO₂/In_{0.53}Ga_{0.47}As at the frequency 1 kHz ~ 100 kHz from V_g= -1 to -2 volts at (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C ,which compared from the distributed border trap model.



Fig. 3.8 The transferred *G-V* map of total experimental *G-F* data for *p*-type Pt/Ti/TMA+Al₂O₃ 5 cycle+ZrO₂/In_{0.53}Ga_{0.47}As at the frequency 1 kHz ~ 100 kHz from V_g = -1 to -2 volts at (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C ,which compared from the distributed border trap model.



Fig. 3.9 The transferred *C-V* map of total experimental *C-F* data for *p*-type Pt/Ti/TMA+Al₂O₃ 10 cycle+ZrO₂/In_{0.53}Ga_{0.47}As at the frequency 1 kHz ~ 100 kHz from V_g = -1 to -2 volts at (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C ,which compared from the distributed border trap model.



Fig. 3.10 The transferred *G-V* map of total experimental *G-F* data for *p*-type Pt/Ti/TMA+Al₂O₃ 10 cycle+ZrO₂/In_{0.53}Ga_{0.47}As at the frequency 1 kHz ~ 100 kHz from V_g = -1 to -2 volts at (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C ,which compared from the distributed border trap model.



Fig. 3.11 The frequency dispersion calculated by using the bulk-oxide traps model (line) and experimental data taken at C_s=0.75μF/cm²(circle) of ALD-TMA/ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs under different PDA conditions with various Al₂O₃ inter-layer (a) 0 cycle (b) 1 cycle (c) 5 cycle (d) 10 cycle. Moreover, the color of black, red, green, and blue indicate as deposited, PDA 300 °C, 400 °C, 500 °C, respectively.



Fig. 3.12 Comparison of the fitted *G-F* map at $C_s=0.75\mu$ F/cm² of ALD-TMA/ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs under different PDA conditions with various Al₂O₃ inter-layer (a) 0 cycle (b) 1 cycle (c) 5 cycle (d) 10 cycle. Moreover, the color of black, red, green, and blue indicate as deposited, PDA 300 °C, 400 °C, 500 °C, respectively.


Fig. 3.13 The frequency dispersion calculated by using the bulk-oxide traps model (line) and experimental data taken at C_s=0.75μF/cm²(circle) of ALD-TMA/ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs with various Al₂O₃ inter-layer under different PDA conditions (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.



Fig. 3.14 Comparison of the fitted *G-F* map at $C_s=0.75\mu$ F/cm² of ALD-TMA/ZrO₂/In_{0.53}Ga_{0.47}As MOSCAPs with various Al₂O₃ inter-layer under different PDA conditions (a) as deposited (b) 300 °C (c) 400 °C (d) 500 °C.

$N_{bt} (10^{19} eV^{-1} cm^{-3})$	As-deposited	PDA 300°C /120s	PDA 400°C /120s	PDA 500°C /120s
Al ₂ O ₃ 0cyc		8.93	17.34	21.72
Al ₂ O ₃ 1cyc	8.34	8.39	14.29	15.62
Al ₂ O ₃ 5cyc	7.16	7.02	10.44	13.65
Al ₂ O ₃ 10cyc	7.00	6.74	8.75	12.37

Table 3.1 Overview of the extraction in border traps density $N_{bt}(10^{19} \text{eV}^{-1} \text{cm}^{-3})$ at E-E_v=0.15 eV

(Cs=0.75 $\mu\,\text{F/cm}^2$) for various Al_2O_3 cycles after FGA under various PDA



Chapter 4

Conclusion

In this thesis, we have investigated the electrical characteristics and interfacial chemistry of $In_{0.53}Ga_{0.47}As$ MOSCAPs with ZrO₂ gate dielectric. At first, we utilize the precursors of ALD, such as TMA or TEMAZ, to passivate the surface before depositing dielectrics. Then, the thermal treatments of various PDA conditions with FGA were employed to observe the effect of interface and oxide properties. From the frequency dispersion and hysteresis, we can find the TMA pretreatment is effective to improve the interface and oxide quality. Moreover, comparing to post-deposition temperatures, PDA 300 °C is the best one than the others. The XPS spectra also shows that the higher area ratio of In_2O_3 to $InAsO_4$, As^{2+} to As_2O_5 and As_2O_3 to As_2O_5 indicate the passivation of the trivalent oxides or lower valence As on the interface and result in the better electrical characteristics.

However, the $ZrO_2/In_{0.53}Ga_{0.47}As$ interfaces still have inferior properties than Al_2O_3 on $In_{0.53}Ga_{0.47}As$, so we incorporate several Al_2O_3 inter-layers to discuss its interface property. From the electrical characteristics of the capacitors, we note that the interface and gate dielectric qualities were much improved by inserting thicker Al_2O_3 inter-layer. The D_{it} at midgap also demonstrates the interface could be passivated within thick Al_2O_3 . With the evidence of XPS spectra, we can clarify that the better interface property is caused by the higher ratio values of the As_2O_3 and In_2O_3 passivation. It might be the thicker Al_2O_3 layers tend to displace the As^{5+} oxidation state to the As^{3+} and As^{2+} . Subsequently, we compare the different PDA conditions at each Al_2O_3 inter-layer. It shows that PDA 300 °C with FGA demonstrates the best property than others under certain conditions like frequency dispersion, hysteresis, and the density of interface states. Furthermore, the XPS spectra also displays that

the area ratio becomes larger as the PDA temperature decreasing. Comparison of electrical characteristics, it indicates if interface exist more As_2O_3 and In_2O_3 components, the properties might be improved.

In addition, the influence of frequency dispersion at high negative gate voltage is caused by oxide traps. To further realize the phenomenon of accumulation region, a distributed border traps model between $In_{0.53}Ga_{0.47}As$ and trap states in the gate dielectrics is developed. Then, we fitted the experimental data with the model and extracted density of trap states N_{bt} quantitatively. Finally, comparing with the aforementioned chapter, we can find it has good consistency with our experimental data.

In the future, we suggest that the double layer of gate dielectrics in our experiment can be replaced by depositing ZrO_2 with O_2 -plasma treatment during the process of atomic-layer deposition, which gate oxide quality may be further improved. Moreover, lower temperature of ALD down to 200 °C or less can be a promising method to suppress the interface states. Finally, we expect the improvable gate stacks on III-V substrates can be fabricated by self-aligned MOSFETs.

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Investigation of Electrical and Interfacial Chemistry Analyses for Atomic-Layer-Deposition ZrO₂/Al₂O₃/In_{0.53}Ga_{0.47}As MOSCAPs