

Interfacial X-ray photospectrometry study of In_{0.53}Ga_{0.47}As under different passivation treatments for metal oxide semiconductor field effect transistor devices

M.F. Mohd Razip Wee^{1,2}, A. Dehzangi², N. Wichmann¹, S. Bollaert¹, Burhanuddin Yeop Majlis²

¹Institute of Electronics Microelectronics and Nanotechnology (IEMN), University Lille 1, 59652 Villeneuve d'Ascq Cedex, France

²Institute of Microengineering and Nanoelectronics (IMEN), Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

E-mail: dehzangi@ukm.my

Published in Micro & Nano Letters; Received on 25th September 2013; Accepted on 28th October 2013

In this reported work, comparison is made of a passivation treatment of a III–V compound semiconductor using ammonia and ammonium sulphide solution. The treatment is applied on In_{0.53}Ga_{0.47}As which is chosen for its high mobility especially in high electron mobility transistors. The samples were treated with various parameters such as precursor, vacuum condition and different chemical solutions. Then, samples were deposited with the high *k*-dielectric Al₂O₃ (4 nm thickness) using the atomic layer deposition technique. Five different passivation treatments were used to give proper comparison. Native oxide elements and contaminants were inspected at the interface of the oxide layer and the substrate using X-ray photospectrometry in different angles (25° and 70°). The results indicate the effectiveness of some treatments to eliminate the oxide of gallium and arsenic with a slight presence of indium oxide.

1. Introduction: The electrical properties and performance of metal oxide semiconductor field effect transistors (MOSFETs) are largely affected by the quality of the interface between the insulator and the semiconductor surface. The presence of interface defects, especially interface trapped charges (D_{it}), is found to degrade the quality of the transistor's performance by allowing a leakage of gate current and the pinning of the Fermi level [1]. Elimination of the surface charges by passivation techniques has already been used to reduce the effect of the D_{it} . Several passivation methods such as wet solution [2], plasma [3] and UV-ozone [4] have been proposed as the solution for this problem.

On the other hand, a requirement for higher mobility and transconductance has diverted the attention of researchers to look for a new material as a replacement for silicon base devices. III–V materials are believed to have enormous potential to be a proper replacement, because their mobility is ten times higher compared with Si. The performance of this material is already proven by its usage in high electron mobility transistors (HEMTs) [5]. Among all the III–V materials, In-enriched In_{0.53}Ga_{0.47}As is one of the most established materials to replace Si in complementary metal oxide semiconductor (CMOS) technology, especially for high speed and low power applications [6]. It has a smaller bandgap ($E_g = 0.74$ eV) compared with Si which makes it more suitable to become a channel material in a transistor. In addition, a search for a compatible insulator for this material is boosted by the introduction of high *k*-dielectrics materials [7] that have already helped further scaling of Si [8]. The integration of III–V and high *k*-material in a device must overcome the problem of the interface issue, such as native oxides and thermally grown oxides.

The deposition technique of dielectric is also critical to determine the quality of the interface to make it compatible with CMOS Si technology, ex-situ atomic layer deposition (ALD) was suggested by several resources [9, 10]. Previous research [11] showed a promising result for a III–V compound semiconductor to achieve a low-interfacial density of states for an oxide deposition using ALD. Several dielectric materials are suggested for In_{0.53}Ga_{0.47}As. Ga₂O₃(Gd₂O₃) [GGO] [12], HfO₂ [13] and Al₂O₃ [9] have already been tested in previous works. In this study, Al₂O₃ is chosen because it produces an excellent result of D_{it} based on the

literature and many groups have employed it as a standard oxide [14, 15]. In terms of thermal and electrical properties, Al is really stable in high temperature (max = 1000°C) with high permittivity ($K = 8.6$ – 9.0) and high bandgap value (9 eV).

Several methods for passivation have already been suggested for In_{0.53}Ga_{0.47}As. Utilisation of silane and ammonia was proposed [16] with the excellent result for D_{it} . A phosphorous passivation on undoped In_{0.53}Ga_{0.47}As using in-situ metal organic vapour phase epitaxy by flowing phosphine has demonstrated an excellent result of D_{it} on InGaAs [17]. Passivation based on sulphur has also been applied especially using ammonium sulphide (NH₄)₂S [18]. The effectiveness of (NH₄)₂S to remove the native oxide of InP, InGaAs, GaAs has already been reported [19, 20].

In this Letter, a combination of the standard passivation method with sulphur passivation is investigated by a double passivation using NH₄OH and (NH₄)₂S on a p-type In_{0.53}Ga_{0.47}As substrate. First, NH₄OH treatment is applied and is followed by (NH₄)₂S. The samples are treated without any specific pretreatment such as HCl. The passivation and the deposition of oxide are executed in vacuum condition. The ALD process is applied in two different methods as thermal and plasma enhanced. During this treatment, rinsing in ammonia plays a major role to suppress the undesirable components of the surface through a slight etching at the surface.

2. Methods: Fig. 1 shows the process flow for this study. First, two layers of p-type In_{0.53}Ga_{0.47}As were epitaxially grown using molecular beam epitaxy (MBE-Riber32P) on an InP substrate. Carbon P-type doping was used on both layers with different concentrations, the first layer with a concentration of 10^{19} cm⁻³ and the second layer or the top layer with the concentration of 10^{17} cm⁻³. Prior to the ALD deposition, surface treatment or passivation is required to eliminate native oxides on the surface by immersing the wafer into a specific solution. We used five different passivation treatments to give a better comparison for the achieving optimised passivation method. In Table 1, more details about the parameters used for each treatment are shown. The solution of NH₄OH was prepared by a dilution of 4 ml of NH₄OH (30%) in 100 ml of deionised (DI) water. A standard treatment by NH₄OH was chosen for four samples. For the last

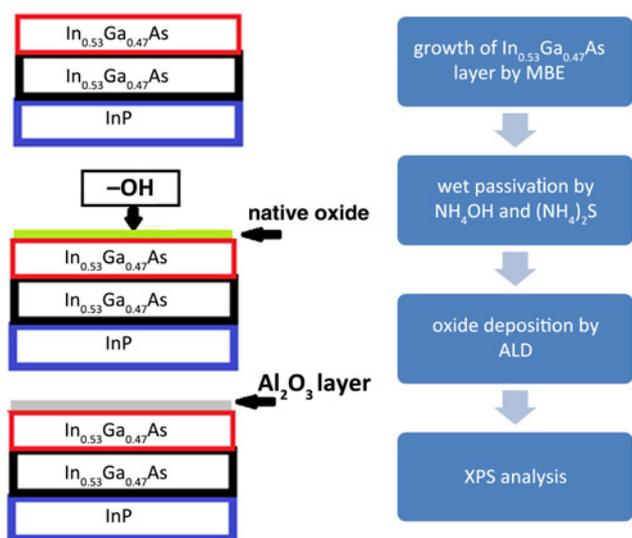


Figure 1 Schematic of process flow for passivation treatment on $In_{0.53}Ga_{0.47}As$

Table 1 Passivation parameter for each sample

Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
H ₂ O rinsing solution	no	yes	yes	yes	yes
oxidising agent	plasma O ₂	plasma O ₂	H ₂ O	H ₂ O	H ₂ O
type of ALD	plasma enhanced	plasma enhanced	thermal	thermal	thermal
atmosphere	vacuum	vacuum	ambient	vacuum	vacuum

sample, The $(NH_4)_2S$ passivation was added during 30 min after the same NH_4OH treatment. The $(NH_4)_2S$ solution was prepared by mixing 5 ml of $(NH_4)_2S$ (20%) in 5 ml of DI water. The next step, was rinsing with DI water for all samples (except sample 1), was applied to remove the solution from the surface before the drying process (with dry nitrogen). To prevent an external contamination in the air ambient and native oxide regrowth, the whole process of passivation was done in the glove box in vacuum condition except for sample 3. Then, from the glove box all the samples were inserted directly into the ALD chamber without any contact with ambient.

A 4 nm layer of aluminium oxide was deposited onto the wafer by ALD (BENEQ-TFS200) using two liquid precursors [trimethyl-aluminium (TMA) and H₂O]. However, the depositions for samples 1 and 2 were slightly different because plasma O₂ was used as the precursor to react with aluminium to form the Al₂O₃ thin layer. The ALD used in our case had two operating modes, the first is thermal ALD using H₂O as oxidising agent, and the second is plasma enhanced ALD (PEALD) with plasma O₂ as the oxidising agent. The interest of coating using plasma is the capability of low temperature deposition of the metal, especially for oxides and nitrides. It has already been reported that Al₂O₃ layer properties were not influenced by the oxidant source at the temperature from 100 to 300°C [21]. However, to facilitate proper comparison, an identical temperature was applied for both cases. During the process, the chamber was heated up to 300°C. Prior to the deposition, an interfacial self-cleaning through the ligand exchange can remove the

oxides from InGaAs substrate. The effectiveness of oxide removal from the surface relied on the choice of metal organic precursor. By using TMA as a precursor, the oxide elimination was successfully done in InGaAs, demonstrating a good performance in term of static measurements for the III–V MOSFET [22].

The interfaces for all samples were analysed in a Vacuum Science Workshop (VSW) surface analysis chamber equipped with VSW 150 XPS to quantify the oxides detected from the InGaAs interface. The spectra of As3d, In4d, In3d and Ga3d were analysed with a monochromatic Al K α X-ray source. From these spectra, the presence of conductive native oxides, such as As₂O₅, As₂O₃, Ga₂O₃ and In₂O₃, as well as contamination from the environment could be quantified. Two different angles (25° and 70°) were used to measure the elements cited above at different depths.

3. Result and discussions: Our focus on XPS measurement is to study the main bulk states of As, Ga and In such as As3d, Ga3d, In3d and In4d spectrums. These states will give significant signals compared with others since they are located at the valence band. Recent study has demonstrated that some of these bulk peaks are not sensitive enough to be measured with XPS using a normal angle [23]. As a precaution, the maximum angle for our measurement is 70°.

The overall results of XPS show quite a similarity for samples 3–5 on the one hand and samples 1 and 2 on the other hand, where no significance difference exists between them. In this matter, the XPS results are depicted here for samples 3–5 all

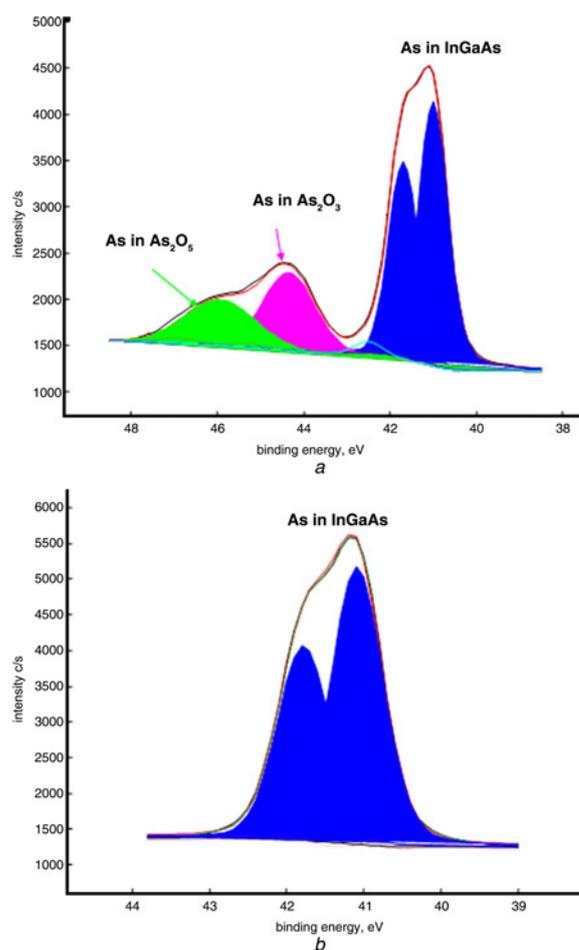


Figure 2 XPS spectra for As3d
a For samples 1 and 2
b For samples 3–5

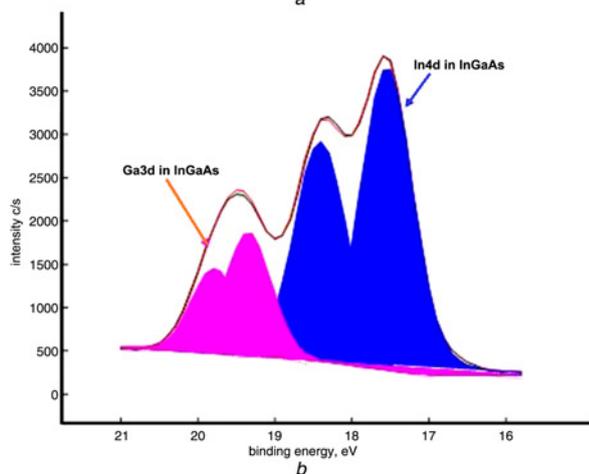
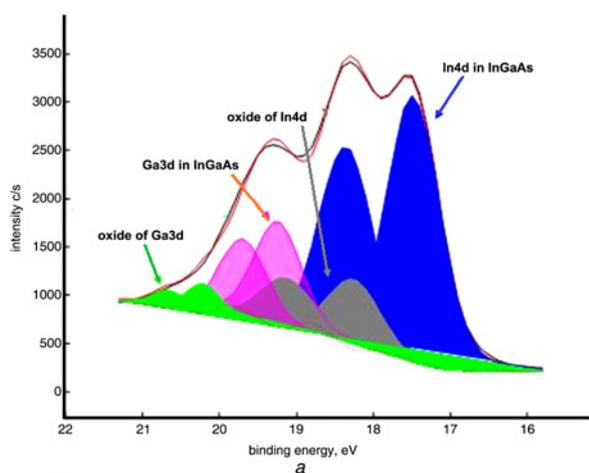


Figure 3 XPS spectra for Ga3d and In4d
 a For samples 1 and 2
 b For samples 3–5

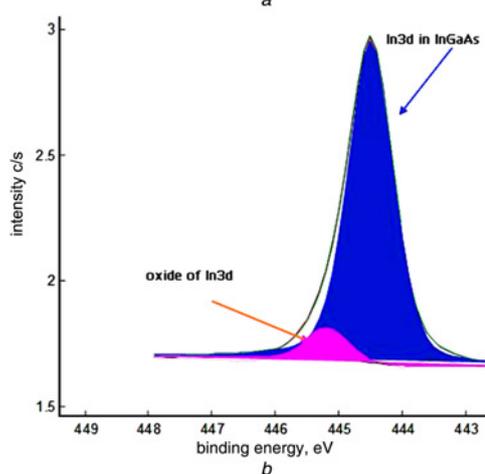
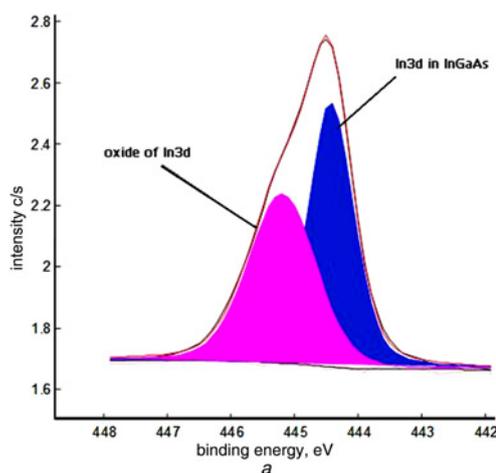


Figure 4 XPS spectra for In3d
 a For samples 1 and 2
 b For samples 3–5

together as well as for samples 1 and 2. Regarding to the treatment methods for samples 1 and 2 (Table 1), it seems that the presence or absence of the H₂O rinsing step is unable to make a significant effect on results. Samples 3–5 give promising results where Ga and As oxide totally disappeared with a small presence of In oxide. However, results from samples 1 and 2 are not really encouraging because the quantity of oxide is quite abundant after the treatment and deposition.

Fig. 2 shows the comparison for spectrum As3d core level lines for all samples at 70°. Fig. 2a is representative for the samples 1 and 2 and Fig. 2b is related to samples 3–5. The native oxides of As exist in two different forms, namely As₂O₃ and As₂O₅, corresponding to As³⁺ and As⁵⁺ as shown in Fig. 2a. As can be seen for samples 3–5 in Fig. 2b, the passivation method was successfully able to remove native oxide of As to be below the detection limit of XPS. A previous report by Hinkle *et al.* [24] stated that ammonia is effective to react against As₂O₅ and eliminate it from the surface. To remove As₂O₃, a self-cleaning mechanism by ligands exchange of TMA is the main element to excite As³⁺ to leave the interface.

Figs. 3a and b demonstrate the XPS results for Ga3d core level lines for all samples at 70°. As can be seen in Fig. 3a, samples 1 and 2 still indicate a presence of Ga and In oxide from spectrum Ga3d and In4d, respectively. The explication of mediocre result from samples 1 and 2 is probably because of the influence of the used oxidising agent, which was plasma O₂ compared to samples 3–5 where H₂O was used. It is worth noting that the choice of oxidant is determined by the type of ALD used.

According to our experiment, thermal ALD has the more suitable result compared with PEALD. A comparative study by Jinesh *et al.*

[25] of Al₂O₃ deposition on silicon by PEALD and thermal ALD shows an improvement of electrical properties for the oxide layer (i.e. lower oxide trap charges, higher tunnel barrier and better dielectric permittivity, $k=8.8$) in PEALD. The explanation for this contrary result is probably related to the metal organic precursor used, and the choice of substrate that lead to a diverse mechanism. An improvement by plasma is possible through a correct choice of precursor and wafer.

The Ga3d spectrum in Fig. 3b indicates a total removal of Ga oxide essentially by NH₄OH for samples 3–5. Osakabe and Adachi [26] have reported the same result for native oxide removal for GaAs by NH₄OH where the surface was transformed into hydrophilic.

The In3d XPS spectra in Fig. 4 indicates the existence of In oxides along with the bulk of In for samples 1 and 2 (Fig. 4a) and less of it in samples 3–5 (Fig. 4b). Fig. 4 shows that the passivation is not sufficient to suppress In oxide in all samples. To remove In oxide, we propose a consecutive treatment by NH₄OH and (NH₄)₂S which was realised in sample 5. In this case, NH₄OH will essentially be able to remove native oxides of Ga and As, and after that the sulphide (NH₄)₂S can eliminate In oxides. As mentioned before, for samples 1 and 2 (as well as samples 3–5), the XPS interpretation indicates no remarkable difference. The quantity of native oxide after the treatment is quite similar for these samples.

One possible reason for this similarity is related to the formation of the monolayer of the hydroxyl group bonded at the surface after NH₄OH treatment [27]. This layer reacts as a protective layer to prevent any chemical reaction of (NH₄)₂S with the surface,

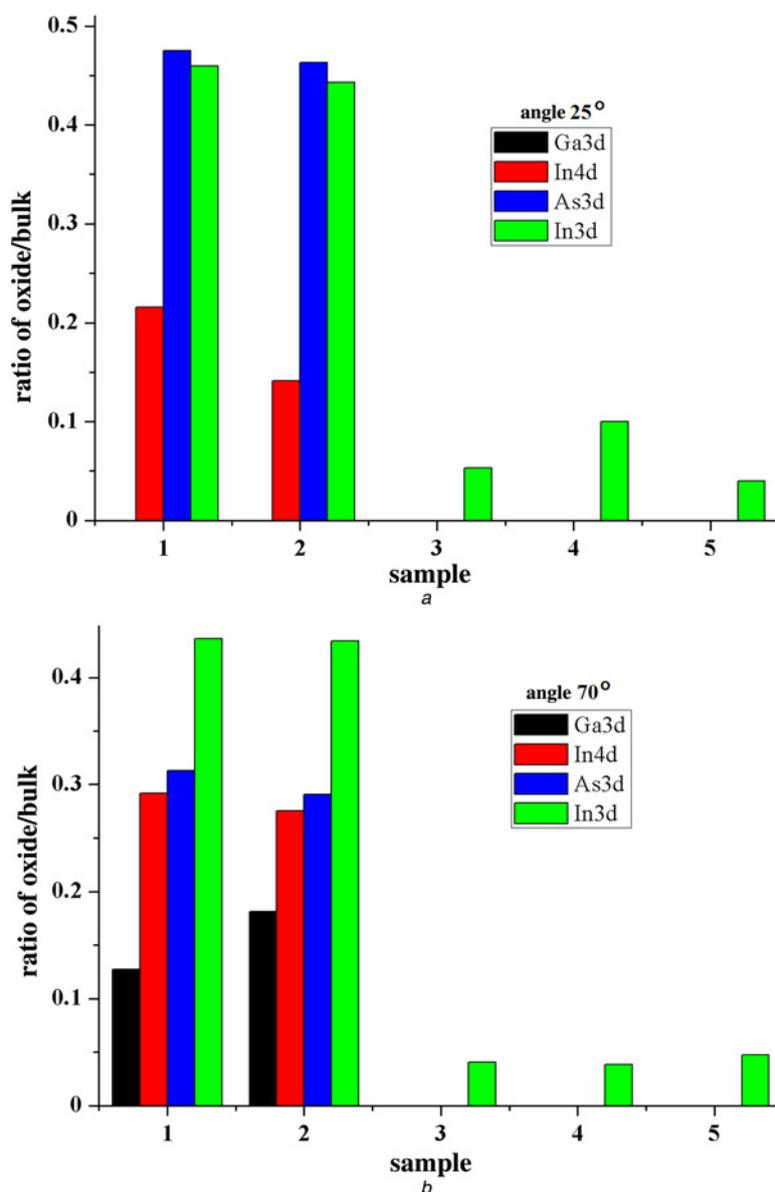


Figure 5 Comparison demonstration of the ratio of oxide/bulk in all examined samples for two angles
 a 25°
 b 70°

especially with sulphur bonds. For sample 5, the absence of air ambient will preserve this OH bonding before a second treatment. We suggest that a stronger concentration of $(\text{NH}_4)_2\text{S}$ would be more effective to obtain a positive result (for sample 5).

In addition to the effect of precursor and $(\text{NH}_4)_2\text{S}$, the impact of air ambient exposure was also investigated through a comparison between samples 3 and 4. Yet, the difference between the XPS results for two samples is unnoticeable. The reason can be regarded as the short exposure time for sample 3 (3 min), which can be longer (≥ 10 min) to make significant difference compared to sample 4 (vacuum). In reported cases [27], in comparison with the air ambient, the vacuum condition has shown a preferable result for NH_4OH etching to remove native oxides, when exposure to the air would cause oxides regrowth back to the surface.

For XPS results, by tilting the sample with respect to the axis of the analyser, since the sampling depth is changed for a given transition, the different data can be detected in different angles because of various compositions with depth.

To investigate the impact of the angle variation on XPS results, two different angles (25° and 70°) were used to measure the

elements at different depths. The angles are associated with the trajectory of the sample surface and the emitted photoelectrons. The summarised details about the ratio of the oxide to bulk for all examined samples for two angles (25° and 70°) are demonstrated in Fig. 5. The ratio of oxide to bulk is determined by calculation of the peak's area of native oxides divided by the area of the bulk substrate peak. Fig. 5 indicates the absence of the oxide ratio of Ga3d, In4d and As3d in samples 3–5, as it is already addressed before for XPS result, where the ratio of oxide to bulk is nearly similar and independent from increasing the angle for all states. Moreover, the results for samples 1 and 2 show that the Ga3d was detected and As3d is decreased in angle 70°. Our observations are in agreement with previous work of InGaAs [28] for Ga concentration reduction near the surface with respect to In and As. In this angle (70°), emitted photoelectrons they are originated from the deeper part close to the interface region while for 25° photoelectrons they are originated from the deposited oxide layer at the surface. The effect of high temperature during the ALD process is more pronounced at the 70° result, since it is originated from the region closer to the InGaAs substrate where the ALD

deposition begins from. This effect will increase the Ga and In oxide, whereas As oxide is decreasing because of oxygen transfer [20].

In this study, the effect of rapid thermal annealing (RTA) is neglected, since the annealing would regrow certain oxides at the interface. For example, As-S bonds start to disappear when the temperature attains 300°C, and at this point the As oxides are likely to be formed [29]. However, Ga-S is really stable at high temperature and can stand up to 500°C [23]. Some studies have already reported the influence of RTA on reduction of the oxide amount [20]. As a matter of fact, a deep consideration of temperature is required before we apply any annealing to the structure. The recent study for investigation of the RTA effect on the performance of self-aligned InGaAs MOSFETs [30] revealed that when the applied temperature was higher than 400°C, a significant negative shift of threshold voltage and degradation in off state performance were extracted. The origin of this problem is the diffusion of the sulphur layer into InGaAs by post-deposition annealing for the temperature more than 400°C, which leads to increment of D_{it} . For further development based on this work for implementing In_{0.53}Ga_{0.47}As MOSFETs, we suggest the last gate process for a better electrical performance. Some considerations have to be taken into account for determination of the process parameter to conquer the effect of undesired doping, such as lowering the thermal budget, sidewall requirement etc.

4. Conclusion: The effect of different passivation treatments were examined on the In_{0.53}Ga_{0.47}As surface with 4 nm Al₂O₃ oxide thickness. From the results, the sample treated with NH₄OH using thermal ALD presents the best result compare with the others. This method has successfully remove oxide of Ga and As with a slight quantity of In oxide remaining. To eliminate the remaining In oxide, an additional treatment is advised along with a further study on the stability of the hydroxyl bonding on the surface. A vacuum condition during the transfer should also be maintained to avoid external contamination.

5. Acknowledgments: The authors acknowledge support for this work provided by the NRA of France (MOS35 project, ANR-08-NANO-022) and the Universiti Kebangsaan Malaysia (grant project DIP-2012-16). M.F. Mohd Razip Wee thanks L. Buchailot, the director of IEMN, R. Buyong and K.S. Siow from IMEN for their great support and assistance.

6 References

- [1] Hinkle C.L., *ET AL.*: 'Detection of Ga suboxides and their impact on III-V passivation and Fermi-level pinning', *Appl. Phys. Lett.*, 2009, **94**, (16), p. 162101
- [2] Lee J.-H., *ET AL.*: 'New method for the electronic and chemical passivation of GaAs surfaces using CS₂', 1996
- [3] Suleiman S.A.B., Lee S.: 'Gate-leakage and carrier-transport mechanisms for plasma-PH 3 passivated InGaAs N-channel metal-oxide-semiconductor field-effect transistors', *J. J. Appl. Phys.*, 2012, **51**, (2), p. 02BF02
- [4] Driad R., *ET AL.*: 'Reduction of surface recombination in InGaAs/InP heterostructures using UV-irradiation and ozone', *Jpn. J. Appl. Phys. 1, Regul. Pap. Short Notes Rev. Pap.*, 1999, **38**, (2 B), pp. 1124–1127
- [5] Lai R., *ET AL.*: 'Sub 50 nm InP HEMT device with Fmax greater than 1 THz', 2007, pp. 609–611
- [6] Irisawa T., *ET AL.*: 'High mobility p-n junction-less InGaAs-OI tri-gate nMOSFETs with metal source/drain for ultra-low-power CMOS applications', 2012, pp. 1–2
- [7] Chang C.H.: 'Interfacial self-cleaning in atomic layer deposition of HfO₂ gate dielectric on In_{0.15}Ga_{0.85}As', *Appl. Phys. Lett.*, 2006, **89**, (24), p. 242911

- [8] Maity N.P., Chakraborty S., Roy M.: 'Silicon and silicon carbide based metal-oxide-semiconductor devices using HfO₂ and SiO₂ gate dielectric', *Int. J. Appl. Eng. Res.*, 2011, **6**, (3), pp. 391–399
- [9] Chang P., *ET AL.*: 'Self-aligned inversion-channel In_{0.53}Ga_{0.47}As metal-oxide-semiconductor field-effect transistors with in-situ deposited Al₂O₃/Y₂O₃ as gate dielectrics', *Appl. Phys. Express*, 2011, **4**, (11), p. 114202
- [10] Xuan Y., Wu Y.Q., Ye P.D.: 'High-performance inversion-type enhancement-mode InGaAs MOSFET with maximum drain current exceeding 1 A/mm', *IEEE Electron Device Lett.*, 2008, **29**, (4), pp. 294–296
- [11] Chiu H.C., *ET AL.*: 'Achieving a low interfacial density of states in atomic layer deposited Al₂O₃ on In_{0.53}Ga_{0.47}As', *Appl. Phys. Lett.*, 2008, **93**, (20), p. 202903
- [12] Hong M., *ET AL.*: 'Novel Ga₂O₃(Gd₂O₃) passivation techniques to produce low Dit oxide-GaAs interfaces', *J. Crystal Growth*, 1997, **175–176**, (PART 1), pp. 422–427
- [13] Lee K.Y., *ET AL.*: 'Molecular beam epitaxy grown template for subsequent atomic layer deposition of high κ dielectrics', *Appl. Phys. Lett.*, 2006, **89**, (22), p. 222906
- [14] Kwo J., Hong M.: 'Research advances on III-V MOSFET electronics beyond Si CMOS', *J. Crystal Growth*, 2009, **311**, (7), pp. 1944–1949
- [15] Xuan Y., *ET AL.*: 'High-performance submicron inversion-type enhancement-mode InGaAs MOSFET with maximum drain current of 360 mA/mm and transconductance of 130 mS/mm'. 65th Annual Device Research Conf., Notre Dame, IN, USA, 2007, 2007, pp. 207–208
- [16] Chin H.C., *ET AL.*: 'Silane and ammonia surface passivation technology for high-mobility In_{0.53}Ga_{0.47}As MOSFETs', *IEEE Trans. Electron Devices*, 2010, **57**, (5), pp. 973–979
- [17] Pal S., *ET AL.*: 'Phosphorous passivation of In_{0.53}Ga_{0.47}As using MOVPE and characterization of Au-Ga₂O₃(Gd₂O₃)-In_{0.53}Ga_{0.47}As MIS capacitor', *Appl. Surface Sci.*, 2005, **245**, (1–4), pp. 196–201
- [18] Skromme B., *ET AL.*: 'Effects of passivating ionic films on the photoluminescence properties of GaAs', *Appl. Phys. Lett.*, 1987, **51**, (24), pp. 2022–2024
- [19] Tang H., *ET AL.*: 'Effect of sulfur passivation on the InP surface prior to plasma-enhanced chemical vapor deposition of SiN', *Semiconductor Sci. Technol.*, 2008, **23**, (3), pp. 035031
- [20] Brennan B., *ET AL.*: 'Optimisation of the ammonium sulphide (NH₄)₂S passivation process on In_{0.53}Ga_{0.47}As', *Appl. Surface Sci.*, 2011, **257**, (9), pp. 4082–4090
- [21] Van Hemmen J.L., *ET AL.*: 'Plasma and thermal ALD of Al₂O₃ in a commercial 200 mm ALD reactor', *J. Electrochem. Soc.*, 2007, **154**, (7), pp. G165–G169
- [22] Huang M.L., *ET AL.*: 'Surface passivation of III-V compound semiconductors using atomic-layer-deposition-grown Al₂O₃', *Appl. Phys. Lett.*, 2005, **87**, (25), pp. 1–3
- [23] Arabasz S., *ET AL.*: 'XPS analysis of surface chemistry of near surface region of epi-ready GaAs(1 0 0) surface treated with (NH₄)₂S_x solution', *Appl. Surface Sci.*, 2006, **252**, (21), pp. 7659–7663
- [24] Hinkle C.L., *ET AL.*: 'GaAs interfacial self-cleaning by atomic layer deposition', *Appl. Phys. Lett.*, 2008, **92**, (7), p. 071901
- [25] Jinesh K.B., *ET AL.*: 'Dielectric properties of thermal and plasma-assisted atomic layer deposited Al₂O₃ thin films', *J. Electrochem. Soc.*, 2011, **158**, (2), pp. G21–G26
- [26] Osakabe S., Adachi S.: 'Chemical treatment effect of (001) GaAs surfaces in alkaline solutions', *J. Electrochem. Soc.*, 1997, **144**, (1), pp. 290–294
- [27] Morota H., Adachi S.: 'Properties of GaP(001) surfaces chemically treated in NH₄OH solution', *J. Appl. Phys.*, 2006, **100**, (5), p. 054904
- [28] Aguirre-Tostado F., *ET AL.*: 'Indium stability on InGaAs during atomic H surface cleaning', *Appl. Phys. Lett.*, 2008, **92**, (17), p. 171906
- [29] Yoshida N., *ET AL.*: 'Surface passivation of In_{0.52}Al_{0.48}As using (NH₄)₂S_x and P₂S₅/(NH₄)₂S', *Jpn. J. Appl. Phys. 1, Regul. Pap. Short Notes Rev. Pap.*, 1994, **33**, pp. 1248–1252
- [30] Gu J., Wu Y., Ye P.: 'Effects of gate-last and gate-first process on deep submicron inversion-mode InGaAs n-channel metal-oxide-semiconductor field effect transistors', *J. Appl. Phys.*, 2011, **109**, (5), p. 053709