

Initial investigation on the impact of in situ hydrogen plasma exposure to the interface between molecular beam epitaxially grown p-Ga_{0.7}In_{0.3}Sb (100) and thermal atomic layer deposited (ALD) Al₂O₃

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Abstract

This work presents, to the best of the authors knowledge, the first experimental findings on the impact of in situ H₂ plasma exposure to the electrical properties of the interface between p-type Ga_{0.7}In_{0.3}Sb and atomic layer deposited Al₂O₃. The effects of trimethyl aluminium (TMA) exposure prior to Al₂O₃ deposition, and of a post gate metal forming gas anneal (FGA) are also investigated. The control sample, which was subjected to an ex situ HCl clean prior to ALD only, demonstrated a capacitance modulation of 36.29 % before FGA. This degraded for samples exposed to the H₂ plasma for all plasma powers investigated. TMA exposure offered no improvement, and significantly increased the frequency dispersion in accumulation for all samples. A post gate metal FGA at 350 °C for 15 minutes was found to substantially improve the interface quality, with the capacitance modulation, frequency dispersion in accumulation and dC/dV improving by as much as 190 %, 91 %, and 170 % respectively.

1. Introduction

Antimonide based compound semiconductors (ABCS) have recently emerged as promising candidates to replace silicon for future complementary metal oxide semiconductor (CMOS) technology nodes [1]. Unlike other III-Vs, ABCS have excellent transport properties for both electrons and holes [2] and could therefore provide a solution for all III-V CMOS. Ga_xIn_{1-x}Sb compounds offer the combined optimum performance for both n and p-type devices, and could facilitate the realisation of common channel inverters [2].

To date, systematic investigations into high-k interfaces on ABCS have been limited to GaSb and InSb [3] only. For the former, ex situ HCl [4] and (NH₄)₂S [5] surface pre-cleans, as well as in situ H₂ plasma pre-treatments [6] have yielded promising results.

In this work, for the first time, the effect of in situ H₂ plasma exposure, prior to high-k atomic layer deposition (ALD), on the p-Ga_{0.7}In_{0.3}Sb–Al₂O₃ interface is investigated. In addition, the effect of in situ trimethyl aluminium (TMA) exposure pre ALD, as well as a post gate metal forming gas (95 % N₂, 5 % H₂) anneal (FGA), both of which have demonstrated positive results on InGaAs [7] and GaSb [6,8], are reported.

2. Experimental

The samples used in this experiment consisted of a 200 nm unintentionally doped relaxed GaSb buffer layer, and a 3.5 μm Ga_{0.7}In_{0.3}Sb device layer, which were grown by molecular beam epitaxy (MBE) on a

semi insulating (SI) GaAs (100) substrate. The device layer comprised a 3 μm contact layer, and a 500 nm capacitor layer, both of which were uniformly p doped with Be, at doping concentrations of 2x10¹⁸ and 2x10¹⁷ cm⁻³ respectively.

All samples were subjected to a wet HCl chemical clean (HCl:RO water, 1:2, for 3 minutes, followed by an IPA rinse) and subsequently loaded into a central vacuum load lock, which is part of a clustered ICP-RIE and ALD tool. The samples were transferred to the load lock in less than 1 minute.

The experimental matrix consisted of subjecting samples to 6 ICP power levels (150 W, 250 W, 500 W, 1000 W, 1500 W and 2000 W) in the ICP-RIE chamber as well as a control sample with no plasma exposure. 150 W was the minimum power that sustained a stable plasma in the ICP tool – lower power plasmas are possible in the ALD tool. The plasma chemistry (H₂:Ar, ~1:7), exposure time (30 minutes) and temperature (150 °C) were based on promising results on GaSb [6]. Subsequent to plasma exposure, samples were transferred under vacuum to the ALD chamber, where 8 nm thermal Al₂O₃ was deposited at 200 °C, using TMA and H₂O. This experimental series was repeated with identical parameters, but additionally included a 600 ms TMA step (30 cycles, 20 ms TMA exposure, 3 s Ar purge), post plasma exposure, pre ALD.

Metal oxide semiconductor capacitors (MOSCAPs) were fabricated using the process flow shown in Fig. 1. To date, following MOSCAP fabrication and measurement, one sample has been subjected to a 15 minute FGA at 350 °C.

3. Results and Discussion

Fig. 2 shows the results of frequency dependent capacitance-voltage (CV) measurements acquired at room temperature (RT) for samples treated with ICP powers up to 250 W, with and without pre ALD TMA exposure. These results were analysed qualitatively in terms of: capacitance modulation at 1 MHz, where $C_{mod} = C_{max} - C_{min} / C_{max}$; frequency dispersion in accumulation; and dC/dV at 1 kHz. These results are summarised in Table 1. It should be noted that for ICP powers > 250 W, no capacitance modulation was observed.

Prior to FGA, none of the samples reached the theoretical minimum capacitance of 193 nF/cm², indicating mid gap Fermi level pinning. Significant capacitance modulation was achieved however, with the control sample without pre ALD TMA exposure demonstrating a 36.29 % change. C_{mod} was found to degrade with H₂ plasma exposure for all powers investigated, and decrease with increasing ICP power. The other metrics did not show a distinct trend. The addition of the TMA exposure prior to ALD offered no improvement to any of the defined metrics, and substantially degraded the frequency dispersion in accumulation for all samples.

The RT frequency dependent CV data for the 250 W sample with pre ALD TMA exposure, post FGA, is shown in Fig. 3. The FGA offered significant improvements with C_{mod} increasing by 190 %, the frequency dispersion reducing by 91 %, and the dC/dV slope increasing by 170 %. No degradation to the leakage current was observed despite the low thermal budget of ABCS [9]. This result is in contrast to results published on InSb [3].

4. Conclusion

This study has demonstrated that the inclusion of in situ H₂ plasma exposure, at plasma powers of more than 150 W in an ICP chamber, prior to the deposition of Al₂O₃ via thermal ALD, degrades the semiconductor-dielectric interface quality compared to the control, which was cleaned ex situ using HCl. TMA exposure prior to ALD was found to deteriorate the interface quality further. These results firstly indicate the potential of HCl as an ex situ pre-treatment on Ga_{0.7}In_{0.3}Sb, and secondly define the parameter space in terms of H₂ plasma power to be further investigated. Finally, a post gate metal FGA at 350 °C for 15 minutes has been shown to substantially improve the interface quality, with no degradation in leakage current.

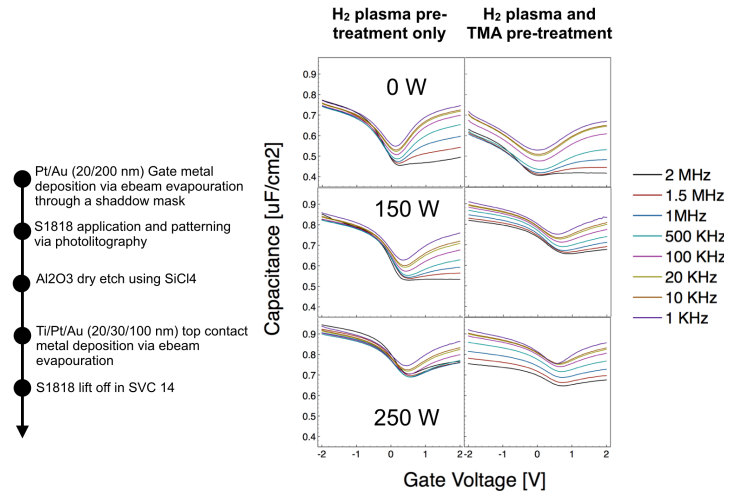


Fig. 1 Overview of MOSCAP fabrication process flow.

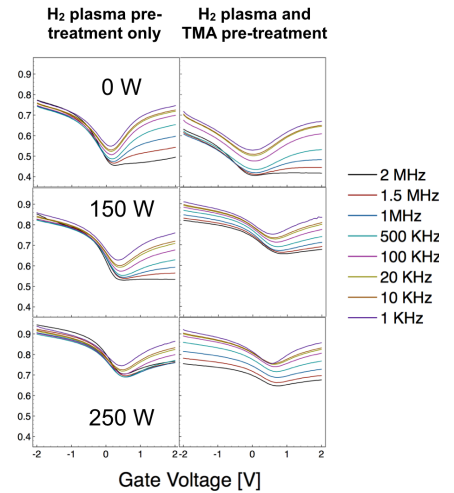


Fig. 2 Room temp. frequency dependent CV measurements for samples with and without TMA pre-treatment, for control samples, and ICP powers of 150 and 250 W.

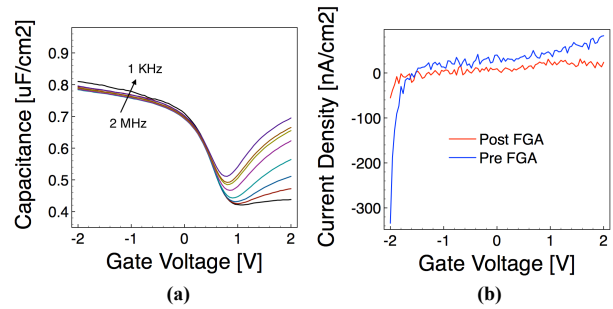


Fig 3. (a) Multi frequency CV measurements and (b) leakage current density of the 250 W sample, with TMA exposure, post 15 minute FGA at 350°C.

Sample	ICP Power (W)	C_{mod} at 1 MHz (%)	$\Delta\%$	Freq. dispersion (1KHz to 1 MHz range)	$\Delta\%$	dC/dV at 1kHz ($\times 10^{-7}$ Fcm ⁻² V ⁻¹)	$\Delta\%$
H ₂ plasma only	0	36.29		2.08		2.31	
	150	33.29	-8.26	4.23	+24.15	2.37	+2.52
	250	23.84	-34.3	1.49	-5.53	1.78	-22.96
H ₂ plasma / TMA	0	29.46	-18.82	14.47	+349.6	1.26	-45.42
	150	20.57	-43.33	8.89	+103.74	1.26	-45.4
	250	15.58	-57.06	15.09	+228.65	1.36	-41.3
	250 + FGA	45.3	+24.84	0.25	-71.3	3.66	+58.25

Table 1 Summary of capacitance modulation, frequency dispersion, and dC/dV for samples treated with H₂ plasma powers up to 250 W, with and without TMA exposure pre ALD. The results were acquired via room temperature, multi frequency CV measurements.

References

- [1] Chau, R. et al, *IEEE Trans. on Nanotech.*, 4(2), 153-158(2005)
- [2] Yuan, Z et al, *Symposium on VLSI Technology* (Vol. 96, pp. 185–186) (2012)
- [3] Trinh, H. D et al, *IEEE Transactions on Electron Devices*, 60(5), 1555–1560 (2013)
- [4] Nainani et al, *J. Appl. Phys.* **109**, 114908 (2011)
- [5] Peralagu et al, *Appl. Phys. Lett.* **105**, 162907 (2014)
- [6] Ruppalt et al, *Appl. Phys. Lett.* **101**, 231601 (2012)
- [7] Carter, A. D, *Appl. Phys. Express*, 4(9), 2000-2002 (2011)
- [8] Cleveland, E. et al, *Applied Surface Science*, 277, 167–175 (2013)
- [9] M. Levinshtein, S Rumyantsev, M Shur, *Handbook Series on Semiconductor Parameters, Volume 2. World Scientific* (1996)