ECS Solid State Letters, **3** (9) N27-N31 (2014)
2162-8742/2014/3(9)/N27/5/$31.00 © The Electrochemical Society

Impact of Q-Time on the Passivation of Al_2O_3/p-$In_{0.53}Ga_{0.47}As$ Interfaces Using Various Surface Treatments

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In this article, we demonstrate the influences of atmosphere exposure duration between extrinsic chemical treatment and ALD chamber loading (*Q-time*) on the passivation effect of the Al_2O_3/p-$In_{0.53}Ga_{0.47}As$ interfaces. With the use of various chemical solutions and TMA pretreatment, nice capacitance-voltage (C-V) characteristics of Al_2O_3/p-$In_{0.53}Ga_{0.47}As$ metal-oxide-semiconductor capacitors (MOSCAPs) were obtained with different *Q-times* before the ALD-Al_2O_3 deposition. This confirms that *Q-time* is not the critical issue determining the Al_2O_3/$In_{0.53}Ga_{0.47}As$ interface quality. X-ray photoelectron spectroscopy (XPS) analyzes in conjunction with the electrical characterizations have implied that the InGaAs native oxides might not play a major role on the interface trap states formation.

Manuscript submitted May 23, 2014; revised manuscript received July 14, 2014. Published July 24, 2014.

The downscaling of complementary metal-oxide-semiconductor (CMOS) may need the integration of III-V semiconductors and related high-k materials, since Si-based devices have reached their physical limitations. Unfortunately, the inherent poor interfacial quality of III-V substrates and high dielectric constant gate oxides lead to the large defect state densities (D_{it}) which results in Fermi level pinning and the loss of channel controlling.[1,2] This issue is still a major challenge that needs to be addressed in spite of many achievements in interface passivation treatments.[3–12] Recently, either ex-situ chemical and in-situ ALD surface treatments of the $In_{0.53}Ga_{0.47}As$ substrates exhibited the strong minority carrier response at inversion region, which means Fermi level can be freely swept through the bandgap of III/V semiconductor.[9–11] Similarly, O'Connor et al.[12] achieved the strong inversion behavior for n, p-$In_{0.53}Ga_{0.47}As$ substrates with sulfur treatment and ALD-Al_2O_3 deposition. They also emphasized the impact of the delay time between the ex-situ chemical surface treatment and the ALD chamber loading (*Q-time*) on the quality of the high-k/III-V interface. The *Q-time* should be limited as low as possible; otherwise, the interfacial quality of high-k/III-V will be degraded. In this study, p-$In_{0.53}Ga_{0.47}As$ substrates were treated by several chemical solutions with different *Q-times* prior to ALD chamber loading. Yet the nice C-V response was still observed even after 24 hours of *Q-time* for the MOSCAP structures studied. In terms of *Q-time* property, our results have supported the conclusion which might stand in contrast with previous studies,[7,8,12] i.e., reduced transfer time (less than few minutes) is not necessarily a prerequisite for an efficient chemical passivation of Al_2O_3/$In_{0.53}Ga_{0.47}As$ interfaces. The nature of interface trap states discussed in this work would facilitate further understanding and passivating of high-k/III-V interfaces.

Experimental

The wafers used were 100 nm p-$In_{0.53}Ga_{0.47}As$ layers (5×10^{17} /cm^3 Be-doped) grown by solid source molecular beam epitaxial on p$^+$-InP substrates. First, the samples were degreased in acetone and isopropanol followed by surface treatment using several chemical solutions as listed in Table I. For *Q-time* studying, two series of samples were conducted with different air exposure duration before introduced to ALD chamber: samples with less than 5 minutes exposure (referred to as 0h samples) and samples with 24 hours exposure (referred to as 24h samples). The in-situ trimethylaluminum (TMA) pretreatments were carried out by ten cycles of TMA/Ar (half an ALD cycle) prior to the growth of 10 nm of Al_2O_3 films. During both TMA pretreatment and deposition processes, the substrates temperature was maintained at 250°C. Then, the samples were post deposition annealed at 450°C in N_2 for 2 min. The gate metal and back side ohmic contact were formed with electron beam evaporation of Ni/Au and AuBe, respectively. Finally, the samples were post metal annealed at 300°C in N_2 for 30 sec.

Results and Discussion

Figure 1 illustrates the multiple-frequency responses of the Al_2O_3/p-$In_{0.53}Ga_{0.47}As$ MOS devices after different chemical treatments and *Q-time*. 24 hours after chemical treatments, there are slightly decreases in the accumulation capacitances (Figs. 1b, 1d, 1f, and 1h) due to the formation of thin oxide layers on $In_{0.53}Ga_{0.47}As$ substrates which was confirmed by XPS results in Fig. 4d, 4f and 4h. Generally, all samples have presented the clear C-V responses as shown by very smooth curves start from accumulation region, through depletion region, to the inversion region (Fig. 1).[9–12] The effective reduction in the mid-gap state density is evidenced by small "weak inversion humps".[13] Moreover, the minimum capacitances at 1 MHz have virtually reached the theoretical value (~185.4 nF/cm^2) for all samples. These results indicate that the Fermi level can be free in movement.[14,15] Thus, it clearly shows that the electrical properties of Al_2O_3/$In_{0.53}Ga_{0.47}As$ structures are independent of the 24 hours *Q-time*.

The C-V hysteresis around flatband voltage at a frequency of 1 MHz and the frequency dispersion in accumulation region of the Al_2O_3/p-$In_{0.53}Ga_{0.47}As$ MOSCAPs with various chemical solutions and *Q-times* are compared in Fig. 2a. The smallest frequency dispersion and hysteresis values observed in sample 1 may be explained by the less contamination being introduced to the oxide layer. Although the frequency dispersion values of samples with chemical 2 and chemical 3 treatments are a little bit higher than that of

Table I. List of surface treatment sequences of the samples investigated.

Chemical treatment sequence	Sample #1	#2	#3	#4
Chemical 1:HCl (3.8%), 2 min.	√	√	√	√
Chemical 2: ATMI-06, 20 min.		√		
Chemical 3: ATMI-08, 20 min.			√	
Chemical 4: $(NH_4)_2S$ (20%):H_2O - (1:3), 20min.				√
DI water	√	√	√	√

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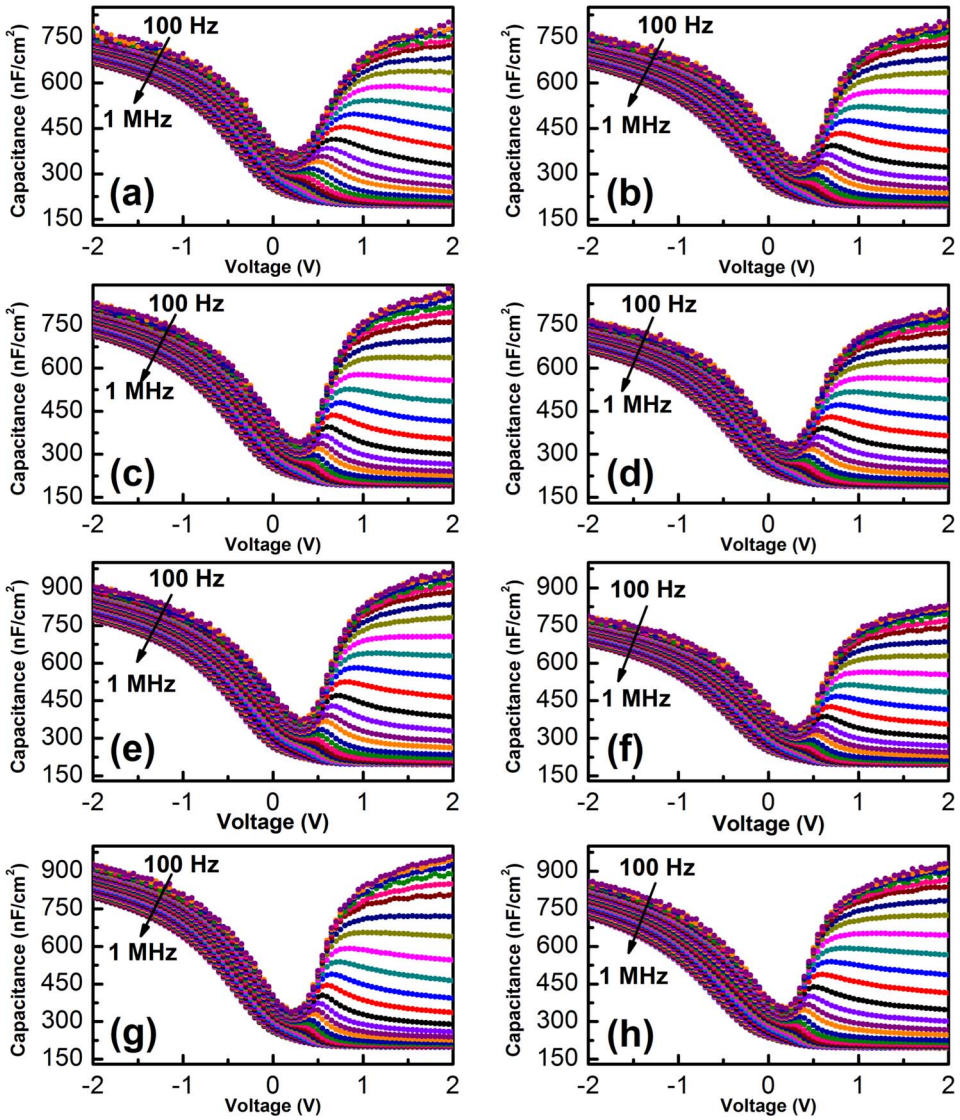

Figure 1. The multifrequency *C-V* responses of Al_2O_3/p-$In_{0.53}Ga_{0.47}As$ MOSCAP structures with different chemical treatments and *Q-times* (a) sample 1, 0h; (b) sample 1, 24h; (c) sample 2, 0h; (d) sample 2, 24h; (e) sample 3, 0h; (f) sample 3, 24h; (g) sample 4, 0h; (h) sample 4, 24h.

chemical 1, they seem to be stable with *Q-time*. The D_{it} distributions of MOS devices estimated from both the conductance method[14] and the Terman method[15] are presented in Fig. 2b. At the trap energy level near midgap, the D_{it} values were extracted by conductance method to be approximately 1.2–1.5 × 10^{12} cm^{-2} eV^{-1}. Besides, the D_{it} values obtained by Terman method are higher than that by conductance method at the same trap energy level as listed in Tables II.

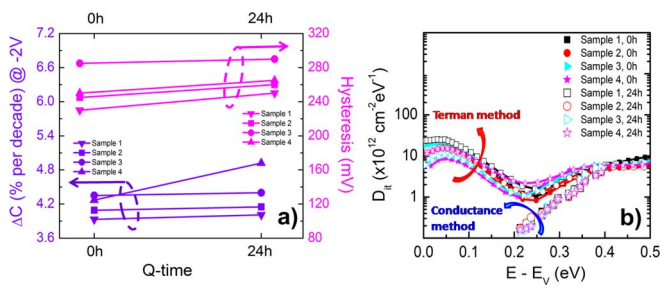

Figure 2. (a) The comparisons of C-V hysteresis around flatband voltage at a frequency of 1 MHz and frequency dispersion in accumulation region of the Al_2O_3/p-$In_{0.53}Ga_{0.47}As$ MOSCAPs with various chemical solutions and *Q-times*. (b) The D_{it} profiles of samples with different chemical treatments and *Q-times*, estimated by the conductance method and the Terman method.

It is reasonable because Terman method probes not only the fast interface traps but also the slow traps near the interface or in the oxide layer.[15] For all of the samples, the effective band bending over a half of InGaAs bandgap (data not show) indicates that an unpinned Fermi level was established. Therefore, this reveals that interfacial quality of the high-k/III-V was preserved with the *Q-time* processing.

The As $2p_{3/2}$, In $3d_{5/2}$, and Ga $2p_{3/2}$ XPS spectra of the native oxide covered and the chemical treated InGaAs surfaces are presented in Fig. 3. With *Q-time* of less than 5 minutes, all of the chemical solutions are effective in restraining the formation of As-O and Ga-O native oxides evidenced by the disappearance of As_2O_5 peak (Fig. 3b, 3d, 3f, and 3h). Compared with other samples, the native oxides of sample 3 and sample 4 seem to be more effectively reduced as shown in Fig. 3f – 3h. After *Q-time* of 24 hours, As and Ga-related oxides increased in most of the samples due to the re-oxidation (Fig. 3c, 3e, 3g, and 3i). The As_2O_5 peak is even observed in the XPS spectral of sample 1 (Fig. 3c). The In-related signals seem to be insignificantly affected by the chemical treatment as indicated by the nearly similar In$3d_{5/2}$ spectrum for all the samples before and after surface chemical treatments (Fig. 3).

Figure 4 illustrates the XPS spectra of the Al_2O_3/p-$In_{0.53}Ga_{0.47}As$ as-deposited structures. Sample 1 with 0h and 24h *Q-time* have exhibited similar expression of As- and Ga-related peaks as can be seen in Fig. 4a and 4b. On the other hand, there are some distinct differences in As-related oxide peaks of samples 2, 3, and 4 with 0h and 24 hours

Table II. The C-V characteristics of the p-Al_2O_3/$In_{0.53}Ga_{0.47}As$ MOSCAPs.

Sample	# 1		# 2		# 3		# 4	
Q-time	0h	24h	0h	24h	0h	24h	0h	24h
Frequency dispersion @ -2V (% per decade)	4.09	4.15	4.35	4.4	4.27	4.92	3.93	4.01
Hysteresis (mV)	245	260	285	290	250	265	215	250
D_{it} @ ~ midgap (cm^{-2}. eV^{-1}), CM*	1.4e12	1.5e12	1.3e12	1.4e12	1.4e12	1.4e12	1.2e12	1.4e12
D_{it} @ ~ midgap (cm^{-2}. eV^{-1}), TM*	3.2e12	3.3e12	3e12	3.4e12	3.6e12	4e12	4.1e12	4.5e12

CM* = Conductance method; TM* = Terman method

Q-time (Fig. 4c – 4h). In case of Ga-related oxides, signals intensities of sample 2 and 3 appeared to be quite stable with *Q-time* values (Fig. 4c – 4f), whereas the intensity signals of sample 4 increased after 24 hours *Q-time* (Fig. 4g and 4h). For *Q-time* below 5 min, a sufficient passivation has been observed on sample 4 as indicated by the noticeable shrinkage of surface native oxides (Fig. 4g). After 24 hours, sample 3 and sample 4 (Fig. 4f and 4h) demonstrated the best inhibition effect against the re-growth of As-related oxides as compared to other samples. In short, the amount of native oxides at Al_2O_3/InGaAs interfaces is not similar for different *Q-times*.

Obviously, the similarity in electrical characteristics of samples with different *Q-times*, as shown in Fig. 1 and 2, suggests that the native oxide may not fully account for the interfacial quality of the devices. Different intensity levels of As $2p_{3/2}$ and Ga $2p_{3/2}$ peaks (Fig. 4) did not result in the different D_{it} values. Recently, Robertson et al.[16] attributed the defect states at high-k/III-V interface to the dangling bonds other than native oxides. Accordingly, these defects would be reduced by both ex-situ chemical and in-situ TMA treatments. It is possible that the native oxides were first removed from the bare surfaces to expose the dangling bonds which were consequently

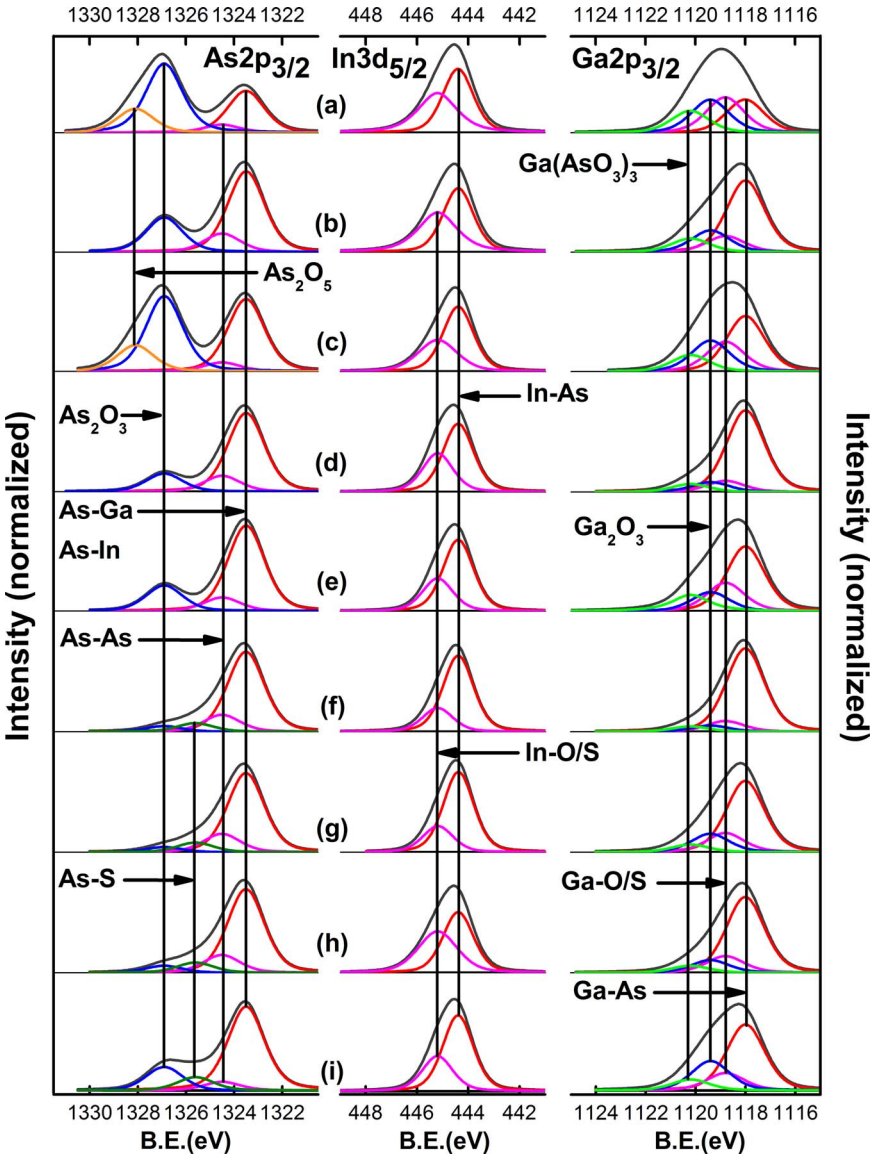

Figure 3. The As $2p_{3/2}$, In $3d_{5/2}$, and Ga $2p_{3/2}$ XPS spectra of (a) bare InGaAs surface; (b) sample 1, 0h; (c) sample 1, 24h; (d) sample 2, 0h; (e) sample 2, 24h; (f) sample 3, 0h; (g) sample 3, 24h; (h) sample 4, 0h; (i) sample 4, 24h.

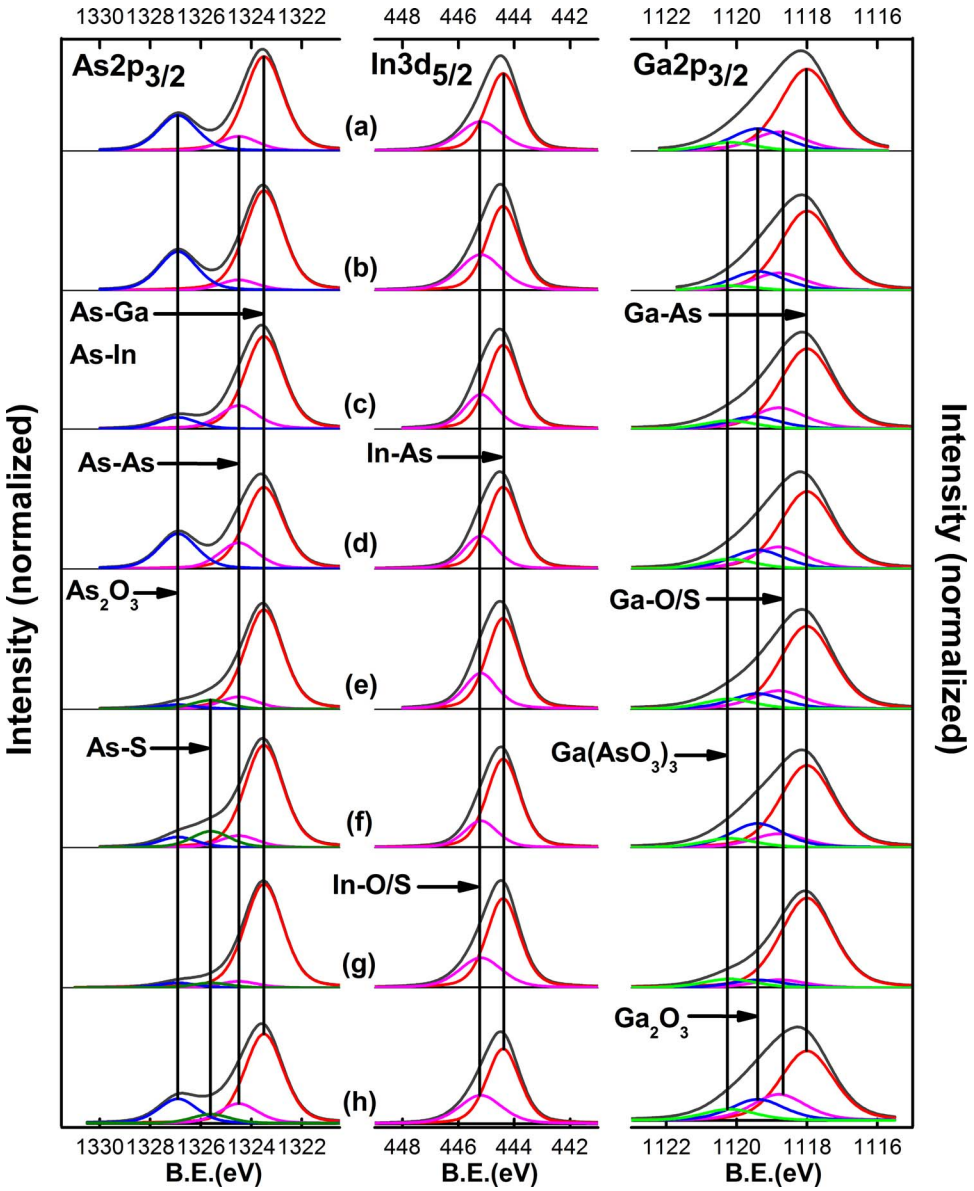

Figure 4. The As $2p_{3/2}$, In $3d_{5/2}$, and Ga $2p_{3/2}$ *XPS* spectra of 1.5 nm Al_2O_3/p-InGaAs with (a) sample 1, 0h; (b) sample 1, 24h; (c) sample 2, 0h; (d) sample 2, 24h; (e) sample 3, 0h; (f) sample 3, 24h; (g) sample 4, 0h; (h) sample 4, 24h.

passivated. The atmosphere exposure, however, is not critical to the passivation effects at least up to 24 hours as illustrated above. Surface states like As and Ga dangling bonds might have contributed to the trapping density; nevertheless, this influence has not been confirmed in this study. Further investigations are required to explain the inherent natures of the interface trap states.

Conclusions

In summary, effective passivation at the Al_2O_3/p-$In_{0.53}Ga_{0.47}As$ interface with the utilization of several chemical solutions and TMA pretreatment has been examined. The electrical properties of Al_2O_3/p-$In_{0.53}Ga_{0.47}As$ MOS structures, with the unpinned Fermi level and low D_{it} value, were independent of the *Q-time* duration up to 24 hours. The native oxides on the III-V surfaces should not be considered as the deciding factor of the interface state formation that degrades the electrical characteristics of high-k/III-V.

Acknowledgment

This work was sponsored by the NCTU-UCB I-RiCE program, Ministry of Science and Technology, Taiwan, and TSMC, ATMI, under grant Number: MOST NSC-103-2911-I-009-302.

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