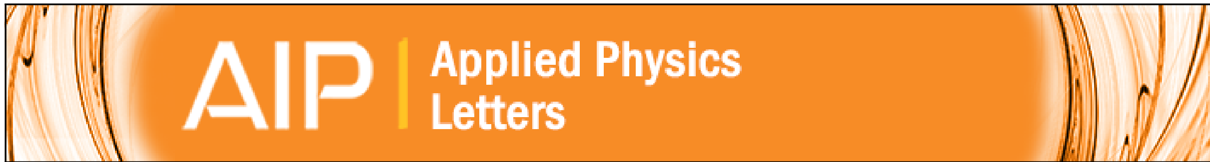

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Citation: Applied Physics Letters **92**, 223501 (2008); doi: 10.1063/1.2937404
View online: http://dx.doi.org/10.1063/1.2937404
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Chemical and physical interface studies of the atomic-layer-deposited Al_2O_3 on GaAs substrates

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(Received 20 January 2008; accepted 7 May 2008; published online 2 June 2008)

In this work, we study the chemical and physical properties of the interface between Al_2O_3 and GaAs for different surface treatments of GaAs. The interfacial layer between the high-κ layer and GaAs substrate was studied using x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The reduction in native oxide layer was observed upon atomic layer deposition of Al_2O_3 on nontreated GaAs using trimethyl aluminum precursor. It was also observed that the sulfide treatment effectively mitigates the formation of the interfacial layer as compared to the surface hydroxylation using NH_4OH. The electrical characteristics of GaAs capacitors further substantiate the XPS and TEM results. © *2008 American Institute of Physics*.
[DOI: 10.1063/1.2937404]

Recently, III-V materials have attracted substantial interest as alternative channel materials to silicon for complementary metal-oxide-semiconductor (CMOS) applications at the 22 nm technology node and beyond. The poor gate oxide/III-V interface quality, however, has long hindered fabrication of high-performance enhancement-mode (E-mode) III-V metal-oxide-semiconductor field-effect transistors (MOSFETs). Hence, there has been tremendous effort to examine the interface between III-V materials and various dielectrics.[1–6] Moreover, the studies on the thermal oxidation of GaAs revealed that the presence of arsenic oxides, which are intrinsically thermally unstable, could give rise to the formation of electronic defects, thereby leading to Fermi level pinning.[7,8]

It is known that atomic layer deposition (ALD) offers a precise control over the uniformity and thickness of the deposited film through a self-limiting reaction.[9] Furthermore, atomic layer deposition could potentially offer the advantage of reducing III-V native oxides by appropriate engineering of the precursor chemistry.[10–12] As a result, ALD could facilitate developing a simple recipe without requiring elaborate *in situ* clean. Nevertheless, integrating ALD high κ on III-V materials necessitates the use of an effective chemical surface treatment protocol. This is to alter the III-V surface properties in order to ensure full surface coverage from the beginning of ALD runs, while preventing the regrowth of native oxides during the *ex situ* sample transfer into the ALD reactor. As a result, we have recently developed an effective chemical surface treatment protocol[13] which has enabled fabrication of inversion-type E-mode GaAs *n*MOSFETs with ALD-Al_2O_3 gate dielectric.[14] This work intends to examine the chemical and physical characteristics of the interface between ALD-Al_2O_3 and GaAs substrates, using x-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM). The correlation between XPS and TEM results, coupled with the electrical properties of the interface, will be further discussed.

In order to investigate the impact of chemical surface cleaning and obtain a better understanding of the role of each chemical treatment in altering the GaAs surface properties, four different sample preparation procedures were devised. It should be noted that all the samples underwent identical processing steps, with the exception of the surface treatment prior to high-κ deposition and postdeposition annealing (PDA) step. In addition, the results of the XPS, TEM, and electrical measurements were obtained from the samples of the same batch. Samples 1, 2, 3, and 4 denote nontreated, HF-last, hydroxylated, and sulfide-treated GaAs substrates, respectively. The details of GaAs surface hydroxylation and sulfide treatment were described elsewhere.[13] The HF-last sample was treated in a 1% diluted HF solution for 1–2 min, whereas the nontreated sample underwent no chemical treatment. After each surface treatment, samples were immediately transferred into a hot-wall ALD reactor, where ~82 Å thick Al_2O_3 was grown by alternating trimethyl aluminum (TMA) and water precursors at 250 °C. Then, samples 3 and 4 were annealed at 550 °C for 5 min in N_2 ambient. Samples 1 and 2, however, did not undergo PDA, due to their relatively poor interface properties. For the XPS samples, the Al_2O_3 layer was thinned down to ~20 Å in a dilute HF solution under a controlled etching condition, in order to enhance corresponding signal/noise ratio for chemical bonds at the Al_2O_3/GaAs interface. For the TEM studies and electrical measurements, GaAs MOS capacitors were fabricated by TaN metal gate deposition using a dc magnetron sputtering system, followed by patterning using standard photolithography and reactive ion etch.

Figure 1 illustrates the As 3*d* and Ga 2*p* XPS spectra of sample 1 before and after Al_2O_3 deposition. The As 3*d* and Ga 2*p* spectra were fitted using Gaussian curves. In order to obtain a valid fit for the As 3*d* spectra, we have considered doublets for As bonding, where they have a peak ratio of 3:2 with a separation of ~0.7 eV. Moreover, all the As 3*d* and Ga 2*p* spectra were normalized with respect to their corresponding As–Ga and Ga–As bonding, respectively. A remarkable reduction in arsenic oxides was observed upon ALD growth of Al_2O_3 using TMA, whereas the reduction in Ga–O bonding was not significant. This facilitates the formation of high quality gate stack on GaAs by reduction in a potentially regrown native oxide layer during the sample

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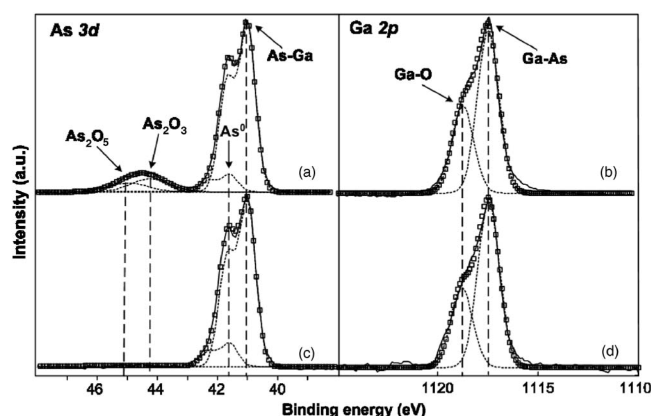

FIG. 1. The As 3*d* and Ga 2*p* XPS spectra of the sample 1 [(a) and (b)] before and [(c) and (d)] after ALD of Al_2O_3, indicating significant reduction in As–O bonding.

TABLE I. Comparing the Al_2O_3/GaAs interfaces of the samples using the XPS and EELS data reveals that the sulfide-treated sample contains the lowest level of an interfacial layer.

		From XPS		From EELS
No.	Sample	As–O (%)	Ga–O (%)	I.L. thickness (nm)
⋯	Bare GaAs	14.6	34.8 ± 0.5	⋯
1	Nontreated	1.6	32.2 ± 0.3	~3.4
2	HF-last	⋯	18.1 ± 0.7	~3.0
3	Hydroxylated	⋯	19.8 ± 0.2	~3.0
4	Sulfide-treated	⋯	16.4 ± 0.3	~1.1

transfer to the ALD reactor after chemical cleaning.

It is widely known that the surface properties of the substrate play an important role in achieving full monolayer coverage during ALD half-cycles, thereby hindering the formation of an undesirable interfacial layer.[15] The XPS studies of the Al_2O_3/GaAs interface revealed that the undesirable interfacial layer mainly consists of elemental arsenic and Ga_2O_3. However, no As–O bonding was evidenced by XPS. The level of each chemical bonding was comparatively estimated for the samples by taking ratio of the area under the corresponding fitted curve for each bonding to the total area of all fitted curves in the corresponding Ga 2*p* or As 3*d* spectra. The results are summarized in Table I for easier comparison. According to the XPS results, the formation of the undesirable interfacial layer appears to be significantly suppressed by sulfide treatment of GaAs, immediately after native oxide removal in dilute HF solution. The XPS studies also reveal that the hydroxylated sample 3 contains the highest level of Ga–O bonding, compared to the other samples.

Figure 2 illustrates the results of the electron energy loss spectroscopy (EELS) for the samples overlaid on their corresponding high annular dark field scanning transmission electron microscopy (HAADF-STEM) micrographs. The cross-sectional TEM studies corroborate the findings of the XPS analysis, where the sulfide treatment appears to give rise to the smallest overlap region among the Ga, As, Al, and O signals, according to the EELS analysis. Moreover, the presence of sulfur was confirmed at the Al_2O_3/GaAs interface. Interestingly, the bright field TEM micrographs of all the samples appear to be almost similar, indicating an abrupt interface between ALD-Al_2O_3 and GaAs (data not shown).

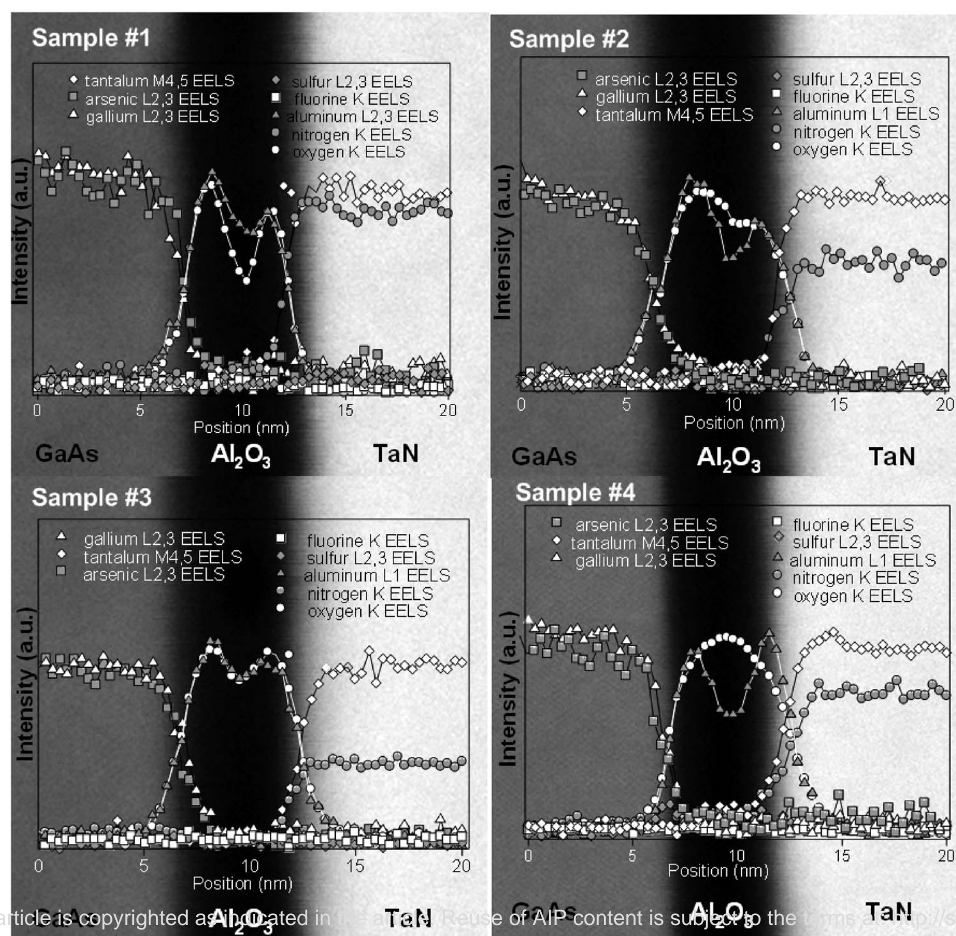

FIG. 2. The HAADF-STEM micrographs superimposed on their corresponding EELS line scan clearly show the differences of the Al_2O_3/GaAs interface for samples 1–4.

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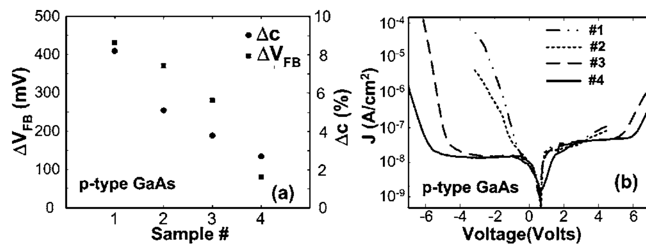

FIG. 3. (a) Variations of the flatband voltage and accumulation capacitance were monitored for the different samples, confirming the effectiveness of the sulfide treatment in improving the Al_2O_3/GaAs interface. (b) The sulfide-treated sample exhibits the best *J-V* characteristics amongst the differently treated samples.

However, the HAADF-STEM micrographs coupled with EELS data reveal the differences in the Al_2O_3/GaAs interface quality among the different samples. The thickness of the interfacial layer for each sample was deduced from the EELS analysis (Table I).

The comparison of the capacitance-voltage characteristics of the samples reveal an improved frequency dispersion behavior for the sulfide-treated sample where the differences of accumulation capacitance ($\Delta C = C_{ox}[10\text{ kHz}] - C_{ox}[1\text{ MHz}]$) as well as the flatband voltage ($\Delta V_{fb} = V_{fb}[10\text{ kHz}] - V_{fb}[1\text{ MHz}]$) at different frequencies are reduced, as shown in Fig. 3(a). Furthermore, the sulfide-treated sample exhibits very low leakage current as compared to the other samples [Fig. 3(b)], confirming the improvement of the interface properties using sulfide treatment scheme.

In summary, we have investigated the physical and chemical characteristics of the ALD-Al_2O_3/GaAs interface using different *ex situ* chemical cleaning methods. It appears that the interface properties were remarkably improved by sulfide treatment of GaAs surface following the native oxide removal in a dilute HF solution. The reduction in GaAs native oxides upon ALD of Al_2O_3 using TMA precursor was also confirmed by XPS and TEM. This interesting phenomenon potentially facilitates *ex situ* processing of GaAs gate stack by reduction in the regrown native oxide during the sample transfer to the ALD reactor.

This work was supported in part by DARPA and Micron Foundation.

[1] M. Passlack, R. Droopad, K. Rajagopalan, J. Abrokwah, R. Gregory, and D. Nguyen, IEEE Electron Device Lett. **26**, 713 (2005).
[2] I. Ok, H. Kim, M. Zhang, C. Kang, S. J. Rhee, C. Choi, S. A. Krishnan, T. Lee, F. Zhu, G. Thareja, and J. C. Lee, IEEE Electron Device Lett. **27**, 145 (2006).
[3] Y. Xuan, H. C. Lin, P. D. Ye, and G. D. Wilk, Appl. Phys. Lett. **88**, 263518 (2006).
[4] D. Shahrjerdi, M. M. Oye, A. L. Holmes, Jr., and S. K. Banerjee, Appl. Phys. Lett. **89**, 043501 (2006).
[5] F. Gao, S. J. Lee, R. Li, S. J. Whang, S. Balakumar, D. Z. Chi, C. C. Kean, S. Vicknesh, C. H. Tung, and D.-L. Kwong, Tech. Dig. - Int. Electron Devices Meet. **2006**, 833.
[6] M. Hong, J. R. Kwo, P-C. Tsai, Y. Chang, M-L. Huang, C-P. Chen, and T-D. Lin, Jpn. J. Appl. Phys., Part 1 **46**, 3167 (2007).
[7] J. G. Ping and H. E. Ruda, J. Appl. Phys. **83**, 5880 (1998).
[8] S. I. Yi, P. Kruse, M. Hale, and A. C. Kummel, J. Chem. Phys. **114**, 3215 (2001).
[9] B. Kellerman, A. Mahajan, N. Russell, J. Ekerdt, S. Banerjee, A. Tasch, A. Campion, J. White, and D. Bonser, J. Aerosol Sci. **13**, 1819 (1995).
[10] M. M. Frank, G. D. Wilk, D. Starodub, T. Gustafsson, E. Garfunkel, Y. J. Chabal, J. Grazul, and D. A. Muller, Appl. Phys. Lett. **86**, 152904 (2005).
[11] M. L. Huang, Y. C. Chang, C. H. Chang, Y. J. Lee, P. Chang, J. Kwo, T. B. Wu, and M. Hong, Appl. Phys. Lett. **87**, 252104 (2005).
[12] C.-H. Chang, Y.-K. Chiou, Y.-C. Chang, K.-Y. Lee, T.-D. Lin, T.-B. Wu, M. Hong, and J. Kwo, Appl. Phys. Lett. **89**, 242911 (2006).
[13] D. Shahrjerdi, E. Tutuc, and S. K. Banerjee, Appl. Phys. Lett. **91**, 063501 (2007).
[14] D. Shahrjerdi, T. Akyol, M. Ramon, D. I. Garcia-Gutierrez, E. Tutuc, and S. K. Banerjee, Appl. Phys. Lett. **92**, 203505 (2008).
[15] Y. Widjaja and C. B. Musgrave, Appl. Phys. Lett. **80**, 3304 (2002).

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