ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/253043139

HfO2 and Al2O3 gate dielectrics on GaAs grown by atomic layer deposition

Article *in* Applied Physics Letters · April 2005

DOI: 10.1063/1.1899745

CITATIONS
323

READS
295

8 authors, including:

Martin M. Frank
IBM

126 PUBLICATIONS **4,733** CITATIONS

SEE PROFILE

Dmitri Starodub
Stanford University

53 PUBLICATIONS **5,144** CITATIONS

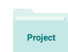
SEE PROFILE

Torgny Gustafsson
Rutgers, The State University of New Jersey

225 PUBLICATIONS **8,454** CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



functionalization View project

SIMS analysis of high-k metal gate stacks View project

All content following this page was uploaded by Eric Garfunkel on 27 July 2015.

The user has requested enhancement of the downloaded file.

HTML ABSTRACT + LINKS

HfO_2 and Al_2O_3 gate dielectrics on GaAs grown by atomic layer deposition

Martin M. Frank[a]
IBM Semiconductor Research and Development Center (SRDC), Thomas J. Watson Research Center, Yorktown Heights, New York 10598

Glen D. Wilk
ASM America, Phoenix, Arizona 85034

Dmitri Starodub, Torgny Gustafsson, Eric Garfunkel, and Yves J. Chabal
Rutgers University, Departments of Physics and Chemistry, and Laboratory for Surface Modification, Piscataway, New Jersey 08854

John Grazul and David A. Muller
Cornell University, Center for Materials Research, Ithaca, New York 14853

(Received 13 January 2005; accepted 26 February 2005; published online 4 April 2005)

High-performance metal-oxide-semiconductor field effect transistors (MOSFETs) on III–V semiconductors have long proven elusive. High-permittivity (high-κ) gate dielectrics may enable their fabrication. We have studied hafnium oxide and aluminum oxide grown on gallium arsenide by atomic layer deposition. As-deposited films are continuous and predominantly amorphous. A native oxide remains intact underneath HfO_2 during growth, while thinning occurs during Al_2O_3 deposition. Hydrofluoric acid etching prior to growth minimizes the final interlayer thickness. Thermal treatments at ~600 °C decompose arsenic oxides and remove interfacial oxygen. These observations explain the improved electrical quality and increased gate stack capacitance after thermal treatments. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1899745]

Metal-oxide-semiconductor field-effect transistors (MOSFETs) on III–V semiconductor would offer a number of advantages over Si-based devices. The higher carrier mobility would lead to faster complementary MOS (CMOS) logic operation, higher breakdown fields would support high-power/temperature applications, band structure engineering would offer design flexibility, and monolithic optoelectronic circuits would likely become manufacturable.

However, MOSFETs on high-carrier-mobility substrates (compound semiconductors as well as germanium) have been elusive due to the lack of high-quality gate insulators, mostly because of the absence of stable passivating native oxides and the high density of slow interface traps (D_{it}) with deposited oxides.[1] For example, Fermi level pinning upon GaAs oxidation has been attributed to oxygen-induced displacement of surface As atoms, where doubly O-coordinated second-layer Ga atoms give rise to gap states.[2] Excess interfacial As occupying As_{Ga} antisite defects causes gap states as well.[2,3] Such As may be formed via decomposition of As_2O_3 in the vicinity of GaAs, resulting from the reaction: $As_2O_3 + 2GaAs \rightarrow Ga_2O_3 + 4As$.[4] Until recently, oxide/III–V interfaces with low D_{it} had to be fabricated by molecular beam epitaxy (MBE) of Ga_2O_3 (where Gd was added to reduce leakage)[1,5] or Al_2O_3.[6] Fermi level unpinning in the $Ga_2O_3/GaAs$ system has been attributed to a $Ga_2O/GaAs$-like interface in which the Ga and As surface atoms are restored to near-bulk charge.[2]

Atomic layer deposition (ALD) or chemical vapor deposition (CVD) is technologically more attractive than MBE. The recent development of high-quality ALD- and CVD-grown high-permittivity (high-κ) gate dielectrics on Si justifies some optimism regarding integration on III–V substrates.[7] Gate stacks for depletion mode MOSFETs with $D_{it} < 10^{12}$ cm^{-2} eV^{-1} were recently fabricated by ALD of Al_2O_3 onto native oxide covered GaAs.[8–10] A 600–650 °C anneal in O_2 minimized current–voltage hysteresis and frequency dispersion, and maximized gate stack capacitance. Transmission electron microscopy (TEM) pointed to a remarkably sharp $Al_2O_3/GaAs$ interface, prompting the speculation that the native oxide is removed during the ALD process. ALD-grown Al_2O_3 also results in good gate stack properties on InGaAs[11] and AlGaN/GaN[12] and may be used to coat compound semiconductor nanowires conformally.[13] By contrast, very few studies have been published regarding the most important high-κ gate dielectric, HfO_2, on III–V semiconductors.[14,15]

In this letter, we characterize the structure and composition of $Al_2O_3/GaAs$ and $HfO_2/GaAs$, to help develop an understanding of the impact of material and processing conditions on the quality of ALD-grown high-κ/III–V stacks. We address successive stages of stack formation: starting surface, temperature ramp-up, ALD process, and anneal. Both Al_2O_3 and HfO_2 were grown on oxide-covered (epiready) and HF-etched GaAs(100). For high-κ dielectric growth, we followed a procedure that recently yielded high-quality $Al_2O_3/GaAs$ gate stacks.[8–10] Depositions were performed using alternating exposures of the common ALD precursors $Al(CH_3)_3 + H_2O$ or $HfCl_4 + H_2O$ in a N_2 carrier gas at 300 °C, using a commercial ASM Pulsar3000™ ALD reactor. C or Al served as caps for microscopy. Films were characterized *ex situ* by scanning TEM (STEM), electron energy loss spectroscopy (EELS), transmission infrared spectroscopy (70° off-normal), medium energy ion scattering (MEIS), and x-ray photoelectron spectroscopy (XPS).

The epiready oxide on GaAs was found by STEM to have a thickness of 20–25 Å [Fig. 1(a)]. The layer is Ga-rich

[a]Electronic mail: mmfrank@us.ibm.com

 © 2005 American Institute of Physics
Downloaded 05 Apr 2005 to 204.52.215.123. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

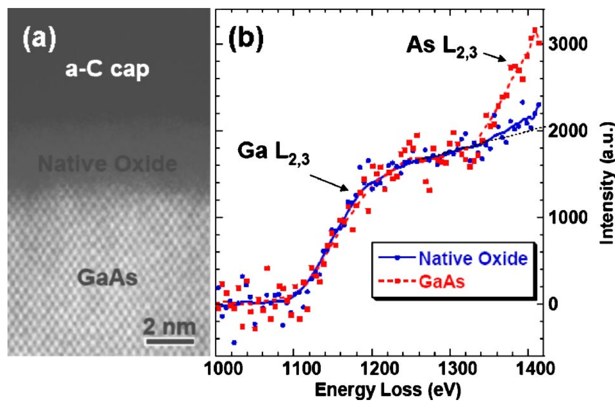


FIG. 1. (Color online) (a) STEM image and (b) STEM-EELS spectra in the Ga and As $L_{2,3}$ regions from C-capped epiready oxide on GaAs(100). Spectra were recorded within the native oxide and in the GaAs substrate.

(As:Ga=0.17), as determined by STEM-EELS [Fig. 1(b)], with an increased As concentration near the GaAs substrate. Areal densities of O and (Ga+As) in the oxide are 3.2 and 3.3×10^{15} cm^{-2}, respectively, as measured by MEIS, consistent with a porous (50% of bulk density) mixture of known oxides containing a high fraction of Ga_2O. In the following, we will denote this substrate Ga(As)O/GaAs. HF-etched substrates, on the other hand, are mostly oxide-free.[16]

During a vacuum preanneal of Ga(As)O/GaAs to the ALD temperature of 300 °C, there is only a 7% reduction in O content, while most surface hydrocarbons desorb (as measured by MEIS, not shown). The lack of any substantial thinning of Ga(As)O during inert anneal to 300 °C is consistent with the higher onset temperatures of reactions in, e.g., thermal (300–390 °C),[17] anodic (430 °C),[4] and wet-chemical/native (320 °C)[18] oxides on GaAs.

The as-deposited high-κ films are continuous, i.e., not islanded, and appear amorphous in TEM images (Fig. 2). Infrared spectroscopy confirms that Al_2O_3 films on Ga(As)O/GaAs are amorphous, as for ALD-grown Al_2O_3 on Si.[19] This is evidenced by absorption features at 720 and 955 cm^{-1} [Fig. 3(a)] which may be assigned to transverse-optical (TO) and longitudinal-optical (LO) phonon modes of amorphous Al_2O_3, respectively. In contrast, for HfO_2 a signal at 700 cm^{-1} and its high-frequency shoulder [Fig. 3(b)] may be attributed to monoclinic HfO_2,[20] indicating crystalline inclusions in an amorphous matrix.

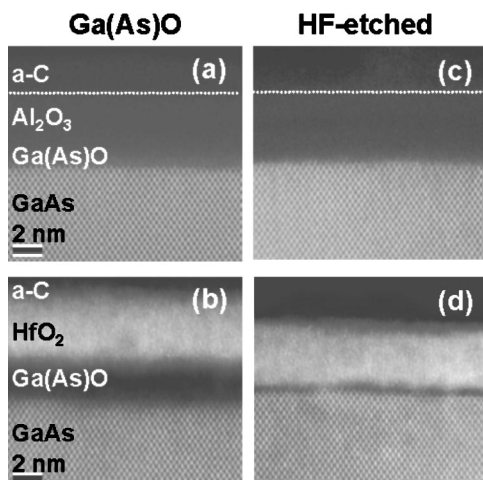


FIG. 2. STEM images from 40 Å Al_2O_3 (top) and HfO_2 (bottom) deposited onto Ga(As)O-covered [(a) and (b)] and HF-etched [(c) and (d)] GaAs(100).

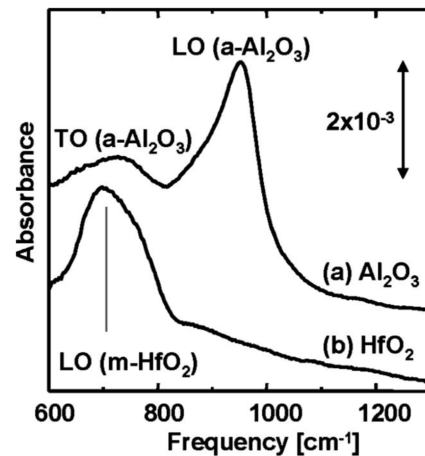


FIG. 3. Transmission infrared spectra from (a) 40 Å Al_2O_3 and (b) 40 Å HfO_2 deposited onto Ga(As)O/GaAs(100). "a" and "m" denote amorphous and monoclinic oxides, respectively.

The structure and composition of the high-κ/GaAs stack depends on the nature of the starting surface. At a target high-κ thickness of 40 Å, the areal densities of metal ions are slightly higher on HF-etched substrates than on oxide-covered substrates (by 14% for Al_2O_3 and by 6% for HfO_2; MEIS, not shown). This may indicate high-κ agglomeration during initial growth on HF-etched GaAs, similar to what has been observed for HF-etched Ge.[21]

Interfacial layer thicknesses after Al_2O_3 and HfO_2 deposition onto Ga(As)O/GaAs are ~10 and 20–25 Å, respectively [Figs. 2(a) and 2(b)]. When native oxide removal by an initial HF wet etch is performed instead, both Al_2O_3 and HfO_2 deposition result in low interfacial layer thicknesses of only 3–8 Å [Figs. 2(c) and 2(d),]. MEIS data support this finding, indicating near-stoichiometric O:Al and O:Hf ratios of 1.51 and 2.04, respectively, for etched substrates, as opposed to oxygen-rich ratios of 1.70 and 2.33 for oxide-covered substrates, with excess oxygen attributed to interfacial Ga(As)O.

The TEM observation of only ~10 Å interfacial oxide for Al_2O_3/Ga(As)O/GaAs indicates that the initial oxide is thinned during the Al_2O_3 ALD growth process. This points to volatilization of Ga(As)O or its conversion into Al_2O_3. By contrast, the HfO_2 growth process does not cause interface thinning, even though the standard Gibbs energies of formation per O atom are nearly identical (Al_2O_3: –527 kJ/mol; HfO_2: –544 kJ/mol) and both higher than for Ga and As oxides.[4,22] The different degree of interface thinning likely is due to the much higher reactivity of $Al(CH_3)_3$ compared to $HfCl_4$, reflected in standard enthalpies of formation of –74 kJ/mol and –990 kJ/mol, respectively.[22,23] Also, ALD reaction with hydroxylated oxides has been shown to be much more favorable for $Al(CH_3)_3$ than for $HfCl_4$.[24–26]

The residual interfacial oxide remains Ga-rich during ALD growth, as shown by STEM-EELS, with As oxides still present in the case of Al_2O_3 on Ga(As)O/GaAs (XPS data in Fig. 4; As oxide signal at 44.8 eV).[27] For all interfaces, TEM images indicate disorder or random strain in the topmost 1–2 GaAs unit cells. The presence of amorphous interfacial GaAs is confirmed by excess visible GaAs in MEIS.

Downloaded 05 Apr 2005 to 204.52.215.123. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

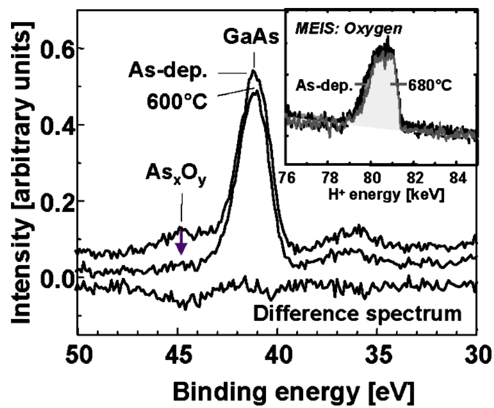


FIG. 4. XPS spectra in the As 3*d* region from 40 Å Al_2O_3 deposited onto Ga(As)O/GaAs(100) before (top) and after (center) vacuum anneal to 600 °C, and difference spectrum (bottom). Inset: MEIS spectra in the oxygen region before and after vacuum anneal to 680 °C.

During vacuum anneals of Al_2O_3 on Ga(As)O/GaAs at 600–680 °C, the As oxides decompose, as detected by changes in the XPS spectrum (Fig. 4).[27] Indeed, most oxygen is removed from the interfacial layer (decrease of 2.5×10^{15} O cm^{-2} for a 40 Å Al_2O_3 film), as evidenced by an intensity drop on the low ion energy side of the MEIS oxygen peak (Fig. 4, inset). This thermal behavior may be rationalized by recalling results for oxidized GaAs surfaces (without a high-κ layer) in inert ambients.[4,17,18,28,29] At 300–460 °C, mixed gallium/arsenic oxides are converted into pure gallium oxide with As precipitates according to the reaction $As_2O_3+2GaAs \rightarrow Ga_2O_3+4As$ (with partial As desorption in the form of As_2 and As_4). At ~475 °C, any Ga_2O present in the film desorbs; and at 580–630 °C, the remaining Ga_2O_3 is volatilized according to $Ga_2O_3+4GaAs \rightarrow 3Ga_2O\uparrow+4As\uparrow$. At similar temperatures, preferential As desorption from the GaAs substrate sets in. Assuming analogous reactions underneath the high-κ layers, including facile outdiffusion of volatile species, a ~600 °C anneal would thus result in (a) a Ga_2O_3-like interfacial layer which, upon continued heating, may be partially or completely removed, and (b) excess interfacial Ga. While we presently do not have any direct experimental evidence for the presence of Ga_2O_3, our findings of As oxide decomposition and oxygen loss are consistent with this reaction scheme.

The role of the O_2 ambient during the 600–650 °C anneal employed in the device studies of ALD-grown Al_2O_3/GaAs stacks[8–10] remains to be explained. Electrical measurements indicate that no additional interfacial oxide grows in O_2.[30] Therefore, the primary difference between mildly oxidizing and reducing anneals may be the oxidation and desorption of excess interfacial Ga. O_2 In addition, may improve high-κ quality, volatilizing As or Ga diffused into the layer and filling detrimental oxygen vacancies.

In conclusion, the interfacial layer thickness and composition in ALD-grown high-κ/GaAs stacks, and thus the device properties, are determined by surface preparation, growth chemistry, and thermal treatments. GaAs oxide remains in place during HfO_2 growth, while partial removal or conversion of the oxide to Al_2O_3 occurs during the Al_2O_3 ALD process. HF etching prior to growth leads to stacks with reduced interfacial layer thickness. Thermal treatments at ~600 °C decompose interfacial As oxides and remove oxygen. This may explain the improved electrical quality and increased capacitance of such structures.

Film growth as well as STEM and infrared analysis were performed at and supported by Bell Laboratories MEIS was performed at Rutgers University and supported by NSF and SRC. M.M.F. was supported by a fellowship from DAAD. D.R.M. and J.G. were supported by the NSF through Cornell's MRSEC Program

[1] M. Hong, C. T. Liu, H. Reese, and J. Kwo, in *Wiley Encyclopedia of Electrical and Electronics Engineering*, edited by J. G. Webster (Wiley, New York, 1999), Vol. 19, p. 87.
[2] M. J. Hale, S. I. Yi, J. Z. Sexton, A. C. Kummel, and M. Passlack, J. Chem. Phys. **119**, 6719 (2003).
[3] W. E. Spicer, Z. Liliental-Weber, E. Weber, N. Newman, T. Kendelewicz, R. Cao, C. McCants, P. Mahowald, K. Miyano, and I. Lindau, J. Vac. Sci. Technol. B **6**, 1245 (1988).
[4] K. Eguchi and T. Katoda, Jpn. J. Appl. Phys., Part 1 **24**, 1043 (1985).
[5] M. Passlack, N. Medendorp, S. Zollner, R. Gregory, and D. Braddock, Appl. Phys. Lett. **84**, 2521 (2004).
[6] J. S. Hwang, C. C. Chang, M. F. Chen, C. C. Chen, K. I. Lin, F. C. Tang, M. Hong, and J. Kwo, J. Appl. Phys. **94**, 348 (2003).
[7] G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **89**, 5243 (2001).
[8] P. D. Ye, G. D. Wilk, J. Kwo, B. Yang, H.-J. L. Gossmann, M. Frei, S. N. G. Chu, J. P. Mannaerts, M. Sergent, M. Hong, K. K. Ng, and J. Bude, IEEE Electron Device Lett. **24**, 209 (2003).
[9] P. D. Ye, G. D. Wilk, B. Yang, J. Kwo, S. N. G. Chu, S. Nakahara, H.-J. L. Gossmann, J. P. Mannaerts, M. Hong, K. K. Ng, and J. Bude, Appl. Phys. Lett. **83**, 180 (2003).
[10] P. D. Ye, G. D. Wilk, B. Yang, J. Kwo, H. J. L. Gossmann, M. Frei, J. P. Mannaerts, M. Sergent, M. Hong, K. K. Ng, and J. Bude, J. Electron. Mater. **33**, 912 (2004).
[11] P. D. Ye, G. D. Wilk, B. Yang, J. Kwo, H. J. L. Gossmann, M. Hong, K. K. Ng, and J. Bude, Appl. Phys. Lett. **84**, 434 (2004).
[12] P. D. Ye, B. Yang, K. K. Ng, J. Bude, G. D. Wilk, S. Halder, and J. C. M. Hwang, Appl. Phys. Lett. **86**, 063501 (2005).
[13] B. Min, J. S. Lee, K. Cho, J. W. Hwang, H. Kim, M. Y. Sung, S. Kim, J. Park, H. W. Seo, S. Y. Bae, M.-S. Lee, S. O. Park, and J.-T. Moon, J. Electron. Mater. **32**, 1344 (2003).
[14] M. Kusaka, M. Hirai, and S. Okazaki, Rep. R. L. Surf. Sci., Okayama U. **4**, 245 (1978).
[15] M. Fanciulli, S. Spiga, G. Scarel, G. Tallarida, C. Wiemer, and G. Seguini, Mater. Res. Soc. Symp. Proc. **786**, E6.14.1 (2004).
[16] S. Adachi and D. Kikuchi, J. Electrochem. Soc. **147**, 4618 (2000).
[17] K. Tone, M. Yamada, Y. Ide, and Y. Katayama, Jpn. J. Appl. Phys., Part 2 **31**, L721 (1992).
[18] F. Schröder, W. Storm, M. Altebockwinkel, L. Wiedmann, and A. Benninghoven, J. Vac. Sci. Technol. B **10**, 1291 (1992).
[19] M. M. Frank, Y. J. Chabal, and G. D. Wilk, Appl. Phys. Lett. **82**, 4758 (2003).
[20] M. M. Frank, S. Sayan, S. Dörmann, T. J. Emge, L. S. Wielunski, E. Garfunkel, and Y. J. Chabal, Mater. Sci. Eng., B **109**, 6 (2004).
[21] A. Delabie, R. L. Puurunen, B. Brijs, M. Caymax, T. Conard, B. Onsia, O. Richard, W. Vandervorst, C. Zhao, M. M. Heyns, M. Meuris, M. M. Viitanen, H. H. Brongersma, M. de Ridder, L. V. Goncharova, E. Garfunkel, T. Gustafsson, and W. Tsai, J. Appl. Phys. **97**, 064104 (2005).
[22] D. R. Lide, *CRC Handbook of Chemistry and Physics*, 85th ed. (CRC, Boca Raton, FL, 2004).
[23] I. Barin and O. Knacke, *Thermochemical Properties of Inorganic Substances* (Springer, Berlin, 1973).
[24] Y. Widjaja and C. B. Musgrave, J. Chem. Phys. **117**, 1931 (2002).
[25] Y. Widjaja and C. B. Musgrave, Appl. Phys. Lett. **80**, 3304 (2002).
[26] L. Jeloaica, A. Estève, M. D. Rouhani, and D. Estève, Appl. Phys. Lett. **83**, 542 (2003).
[27] C. C. Surdu-Bob, S. O. Saied, and J. L. Sullivan, Appl. Surf. Sci. **183**, 126 (2001).
[28] T. Van Buuren, M. K. Weilmeier, I. Athwal, K. M. Colbow, J. A. Mackenzie, T. Tiedje, P. C. Wong, and K. A. R. Mitchell, Appl. Phys. Lett. **91**, 424 (1991).
[29] C. E. C. Wood, K. Singer, T. Ohashi, L. R. Dawson, and A. J. Noreika, J. Appl. Phys. **54**, 2732 (1983).
[30] G. D. Wilk and P. D. Ye (unpublished).

Downloaded 05 Apr 2005 to 204.52.215.123. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp
View publication stats