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In situ study of surface reactions of atomic layer deposited $La_xAl_{2-x}O_3$ films on atomically clean $In_{0.2}Ga_{0.8}As$

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The surface reactions of $La_xAl_{2-x}O_3$ ultrathin films deposited on atomically clean $In_{0.2}Ga_{0.8}As$ by atomic layer deposition are studied by *in situ* high resolution x-ray photoelectron spectroscopy. Using 1:2 alternating cycles of La_2O_3 and Al_2O_3 results in a La:Al concentration ratio of 1:10. We found that the $La_xAl_{2-x}O_3$/InGaAs interface consisted of interfacial Ga-suboxides and As–As bonds but no As- or In-oxides were detected. This suggests an interface formed by Ga–O–Al and Ga–O–La bonds from the precursor reaction. © *2008 American Institute of Physics*.
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The search for a suitable high-κ dielectric on III-V high-mobility substrates for surface channel metal-oxide-semiconductor (MOS) applications has led to resurgence in interest of interface studies. For scaled structures beyond 20 nm gate lengths, the dielectric constant for Al_2O_3 ($\kappa \sim 9$) can be enhanced by the addition of other high-κ oxides (HfO_2 or La_2O_3) while preserving its useful thermal stability.[1,2] Recent reports have investigated molecular beam deposited[3] $LaAlO_3$ and atomic layer deposition (ALD) of $HfAlO_3$ on InGaAs,[4] due to the higher electron mobility and mitigation of Fermi level pinning problems associated with GaAs surface states impacting MOS devices.[5–7]

Differences in the initial surface leads to different reaction channels and therefore to different interface bond arrangements.[8,9] The nucleation of ALD grown Al_2O_3 can depend strongly on the availability of surface–OH groups rather than on the deposition conditions.[10] Lim *et al.* reported the deposition of $LaAlO_3$ (LAO) films on Si using a La amidinate precursor (tris(*N*-*N'*-diisopropylacetamidinato)La $[(^iPr_2\text{-amd})_3\text{-La}]$) and water.[11] They reported a low C contamination ($\sim 1\%$) and no self-decomposition below 350 °C.

In this letter we report on the surface chemical reactions of $La_xAl_{2-x}O_3$ and Al_2O_3 deposited on atomically clean InGaAs substrates by ALD. A recently developed La-amidinate precursor[12] (tris(*N*-*N'*-diisopropylformamidinato)La $[(^iPr_2\text{-fmd})_3\text{-La}]$) together with water is employed for La_2O_3 deposition and trimethyl aluminum (TMA) with water for Al_2O_3. *In situ* ALD and x-ray photoelectron spectroscopy (XPS) analyses are used to study the interface bonding arrangement and the relevant reaction paths are discussed as well.

The $1 \times 1\ cm^2$ substrate consisted of a 13.5 nm $In_{0.2}Ga_{0.8}As$ layer grown by molecular beam epitaxy[13] on a semi-insulating GaAs(001) wafer with an intermediate 535 nm thick GaAs buffer layer. The InGaAs and GaAs buffer layers were doped with Si (*n*-type, $1 \times 10^{17} cm^{-3}$). The InGaAs native oxides were removed using an *in situ* atomic H treatment (AHT) at a substrate temperature of 450 °C.[14] This surface preparation method provides an atomically clean InGaAs surface reconstructed (2×4). After the surface cleaning, either 1.4 or 10 nm $La_xAl_{2-x}O_3$ films were deposited *in situ* using an integrated SUNALE™ ALD reactor.[15] For comparison, a 1 nm thick Al_2O_3 film was deposited under identical ALD conditions on an InGaAs sample separately. The $La_xAl_{2-x}O_3$ ALD deposition was carried out at a substrate temperature of 200 °C to minimize the thermal desorption of volatile As and In in a base pressure of flowing N_2 of 10 mbar. The $La_xAl_{2-x}O_3$ film was deposited by repeating 1 cycle of La_2O_3 (i.e., La precursor+water) and 2 cycles of Al_2O_3 (i.e., Al precursor+water+Al precursor+water) for a total of five times. The integrated ALD reactor, transfer chambers, and XPS system enable the interrogation of the surface without spurious contamination.[16] The XPS data were obtained using an Al $K\alpha_1$ monochromatic x-ray source (0.25 eV line width) and a hemispherical analyzer (pass energy=15 eV) equipped with seven Channeltron® detectors.[17] The take-off angle from the substrate surface was 45°, with an analyzer acceptance angle of 16°. The deconvolution of XPS spectra was performed self-consistently using the software AANALYZER (Ref. 18) with fixed values for parameters such as Lorentzian/Gaussian ratios, spin-orbit splitting, and branching ratios, which are either known or determined directly from the atomically clean InGaAs substrate.[14]

Figure 1 shows the Al 2*p* and O 1*s* XPS spectral regions for a 1.4 nm thick $La_xAl_{2-x}O_3$ film grown using alternating cycles of La_2O_3 and Al_2O_3 on atomically clean $In_{0.2}Ga_{0.8}As$ as well as the comparison spectra for the 1 nm thick pure Al_2O_3.[19] The binding energy of the Al 2*p* (74.9 eV) is consistent with O–Al–O bonding environment.[20,21] The O 1*s* shows two peaks for the pure Al_2O_3 films (at 531.6 and 533.6 eV) and three peaks for the $La_xAl_{2-x}O_3$ film (531.6, 533.0, and 530.0 eV). The first peak is as attributed to oxygen in the Al–O–Al bonds,[20,21] and the second to Al–O–H and La–O–H bonds.[22,23] The third peak, appearing only in the $La_xAl_{2-x}O_3$ film, is chemically shifted by −1.6 eV with respect to the Al–O–Al peak and is identified as oxygen forming Al–O–La bonds. The chemical shift is likely caused by an additional charge transfer[24] from the La to the O atom as the Al and La atoms possess different electronegativities (1.61 and 1.10, respectively).[25] No La–O–La bonding (528.8 eV) is detected.[26] The O 1*s* in Fig. 1 shows no significant difference in the observed amount of hydroxides be-

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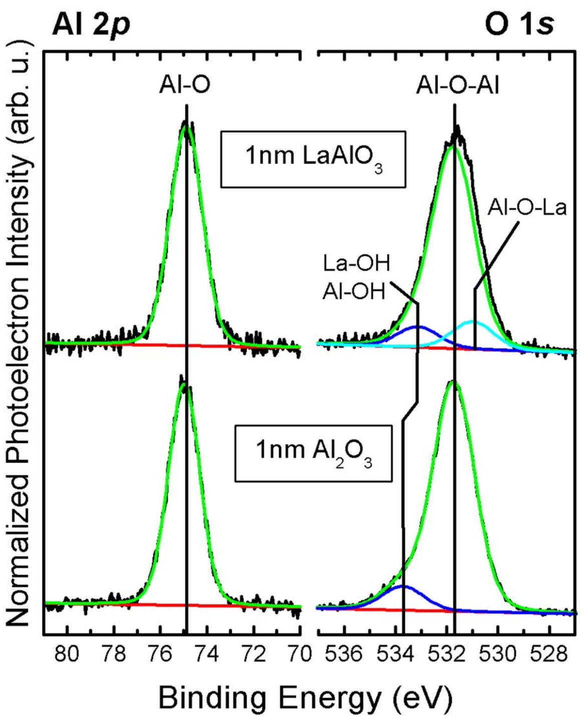

FIG. 1. (Color online) Normalized Al 2p and O 1s XPS peaks for 1 nm of $LaAlO_3$ vs 1 nm of Al_2O_3. In both cases Al 2p shows a single chemical component around 74.9 eV corresponding to fully oxidized Al. O 1s shows a main peak around 531.7 eV corresponding to La–O–Al and Al–O–Al bond arrangements for $LaAlO_3$ and Al_2O_3, respectively. The small feature at 2 eV above corresponds to hydroxyl groups.

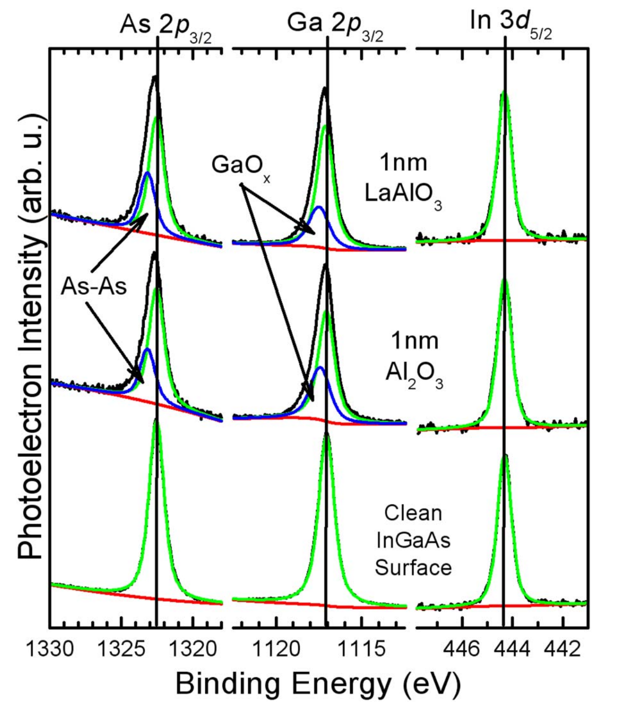

FIG. 2. (Color online) As $2p_{3/2}$, Ga $2p_{3/2}$, and In $3d_{5/2}$ showing the surface reaction at the initial growth of $LaAlO_3$ vs Al_2O_3. The formation of As–As and Ga-suboxides occurs in a similar manner for the two films. The formation of In oxide is not observed.

tween the two samples. From the XPS analysis, the Al–OH amount is ~10% of the total oxygen in the film and is attributed to residual water incorporated during the ALD growth at 200 °C.

The total C content detected in the films (not shown) measured by the XPS C 1s feature to be ~4% for the 10 nm LAO films. For the 1.4 nm LAO film, C–O, C–O–H, and C–C bondings were detected, while the thicker 10 nm LAO film indicated the presence of C–O and/or C–O–H bonding without any observation of carbonate peaks. By comparison, XPS measurement of the Al_2O_3 film indicates the presence of C–C bonding with a C concentration ~4%. We note that these levels of C are somewhat higher than previously reported secondary ion mass spectroscopy results for La(^{i}PrAMD)$_3$ on Si at 300–330 °C,[11] and may be attributed to the lower deposition temperature employed here for the InGaAs substrates.

Figure 2 shows the XPS spectra of the As $2p_{3/2}$, Ga $2p_{3/2}$, and In $3d_{5/2}$ for the clean InGaAs surface (bottom), 1 nm Al_2O_3/InGaAs (middle), and 1.4 nm $La_xAl_{2-x}O_3$/InGaAs (top). The In, Ga, and As peaks in the clean substrate show a single chemical component that is free of detectable surface oxides and As–As bonds as a result of the AHT.[14] After the deposition of 1 nm of Al_2O_3 or $La_xAl_{2-x}O_3$, the In $3d_{5/2}$ region still shows a single chemical component (444.2 eV), indicating that the In-deficient surface[14] results in no In substrate reaction with the overlying oxide.

In contrast, the Ga 2p region shows an additional chemical component at 0.4 eV above the Ga-bulk component and is associated with the formation of Ga-suboxide.[27,28] The chemical shift found here is substantially lower than in Ga_2O_3 suggesting the formation of a Ga-suboxide most likely in the following bond environment: substrate-Ga–O–Al (or La).[28] Similarly, the As $2p_{3/2}$ shows an additional component at 0.63 eV above the position of the As-bulk peak (1322.4 eV) and is associated with As–As bonding.[27] The area ratio of the nonbulk/bulk Ga and As components are 0.31 and 0.49, respectively. Assuming that these chemical species are confined at the interface forming a layer, the above amounts correspond to a full monolayer for each case.[29] Given the amounts of reacted Ga and As at the oxide-substrate interface and chemical bonding detected, we deduce that the reacted interface is chemically abrupt.[14]

Figure 3 shows the Al 2p, O 1s, and La 3d peaks comparing 1.4 nm versus 10 nm thick $La_xAl_{2-x}O_3$ films.[30] Oxidized Al and La species are evident in both films, with the expected XPS satellite structure for La.[31] The relative atomic concentrations were calculated using calibrated atomic sensitivity factors obtained using XPS and Rutherford backscattering spectroscopy from sputter deposited $LaAlO_3$ thick films. From the calculated atomic concentrations the anion to cation atomic ratio is 3:2. The Al:La atomic ratio is 11.5 which gives an $x=0.16$ for $La_xAl_{2-x}O_3$.

In conclusion, we have shown that the ALD growth of $La_{0.16}Al_{1.84}O_3$ and pure Al_2O_3 on atomic hydrogen-treated InGaAs results in similar interface bonding arrangement while producing the equivalent of one monolayer of As–As bonding and Ga–O–Al(La) bridging between the substrate and the film. The employment of an atomically clean InGaAs substrate and ALD deposition of $La_xAl_{2-x}O_3$ using TMA/water and (^{i}Pr$_2$-fmd)$_3$La/water chemistry results in the formation of a single monolayer interfacial layer.

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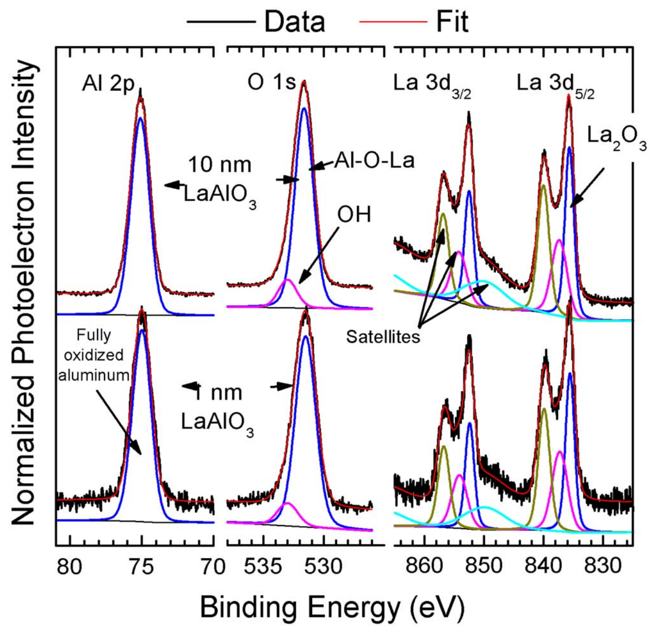

FIG. 3. (Color online) Al $2p$, O $1s$, and La $3d$ comparison of 1 vs 10 nm $LaAlO_3$ films. There are no detectable differences in the $LaAlO_3$ films composition or chemical bonding. The atomic composition calculated from XPS is $La_{0.03}Al_{0.37}O_{0.60}$.

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[1]P. Sivasubramani, M. J. Kim, B. E. Gnade, R. M. Wallace, L. F. Edge, D. G. Schlom, H. S. Craft, and J.-P. Maria, Appl. Phys. Lett. **86**, 201901 (2005).
[2]L. F. Edge, D. G. Schlom, P. Sivasubramani, R. M. Wallace, B. Holländer, and J. Schubert, Appl. Phys. Lett. **88**, 112907 (2006).
[3]N. Goel, P. Majhi, W. Tsai, M. Warusawithana, D. G. Schlom, M. B. Santos, J. S. Harris, and Y. Nishi, Appl. Phys. Lett. **91**, 093509 (2007).
[4]T. Yang, Y. Xuan, D. Zemlyanov, T. Shen, Y. Q. Wu, J. M. Woodall, P. D. Ye, F. S. Aguirre-Tostado, M. Milojevic, S. McDonnell, and R. M. Wallace, Appl. Phys. Lett. **91**, 142122 (2007).
[5]L. J. Brillson, M. L. Slade, R. E. Viturro, M. K. Kelly, N. Tache, G. Margaritondo, J. M. Woodall, P. D. Kirchner, G. D. Pettit, and S. L. Wright, Appl. Phys. Lett. **48**, 1458 (1986).
[6]G. Brammertz, M. Heyns, M. Meuris, M. Caymax, and D. Jiang, Microelectron. Eng. **84**, 2154 (2007).
[7]Y. Xuan, P. D. Ye, and T. Shen, Appl. Phys. Lett. **91**, 232107 (2007).
[8]C. L. Hinkle, A. M. Sonnet, E. M. Vogel, S. McDonnell, G. J. Hughes, M. Milojevic, B. Lee, F. S. Aguirre-Tostado, K. J. Choi, H. C. Kim, J. Kim, and R. M. Wallace, Appl. Phys. Lett. **92**, 071901 (2008).
[9]F. S. Aguirre-Tostado, M. Milojevic, K. J. Choi, H. C. Kim, C. L. Hinkle, E. M. Vogel, J. Kim, T. Yang, Y. Xuan, P. D. Ye, and R. M. Wallace, Appl. Phys. Lett. **93**, 061907 (2008).
[10]R. L. Puurunen, J. Appl. Phys. **97**, 121301 (2005).
[11]B. S. Lim, A. Rahtu, P. de Rouffignac, and R. G. Gordon, Appl. Phys. Lett. **84**, 3957 (2004).
[12]The La precursor is provided by Rohm and Haas Electronic Materials LLC.
[13]The InGaAs/GaAs epitaxial structure was grown by *Intelliepi*.
[14]F. S. Aguirre-Tostado, M. Milojevic, C. L. Hinkle, E. M. Vogel, R. M. Wallace, S. McDonnell, and G. J. Hughes, Appl. Phys. Lett. **92**, 171906 (2008).
[15]See: http://www.picosun.com/.
[16]R. M. Wallace, ECS Trans. **16**, 255 (2008).
[17]Omicron Nanotechnology: http://www.omicron.de.
[18]AANALYZER is a software for XPS peak deconvolution. See: http://www.qro.cinvestav.mx/~aanalyzer.
[19]The Al_2O_3 was deposited *in situ* separately on $In_{0.2}Ga_{0.8}As$ using ten consecutive cycles of TMA and de-ionized water pulses to form an ~1 nm thick film.
[20]O. Renault, L. G. Gosset, D. Rouchon, and A. Ermolieff, J. Vac. Sci. Technol. A **20**, 1867 (2002).
[21]D. Leinen, A. Fernandez, J. P. Espinos, J. P. Holgado, and A. R. Gonzalez-Elipe, Appl. Surf. Sci. **68**, 453 (1993).
[22]M. R. Alexander, G. E. Thompson, and G. Beamson, Surf. Interface Anal. **29**, 468 (2000).
[23]A. Nylund and I. Olefjord, Surf. Interface Anal. **21**, 283 (1994).
[24]P. S. Bagus, F. Illas, G. Pacchioni, and F. Parmigiani, J. Electron Spectrosc. Relat. Phenom. **100**, 215 (1999).
[25]*CRC Handbook of Chemistry and Physics*, edited by D. R. Lide 84th ed. (CRC, Boca Raton, FL, 2004), pp. 9–74.
[26]T. L. Barr, J. Phys. Chem. **82**, 1801 (1978).
[27]S. Arabasz, E. Bergignat, G. Hollinger, and J. Szuber, Appl. Surf. Sci. **252**, 7659 (2006).
[28]S. Ingrey, W. M. Lau, and N. S. McIntyre, J. Vac. Sci. Technol. A **4**, 984 (1986).
[29]The intensity ratio of a monolayer is calculated using the effective attenuation lengths obtained from the EAL-NIST database and the following formula: $I_{film}/I_{substrate}=1=1\ \exp(d/\lambda \cos\theta)$, where d is the interplanar distance, λ is the EAL and θ is the take-off angle measured from the surface plane.
[30]The atomic sensitivity factors found for La $3d_{5/2}$, Al $2p$, and O $1s$ are 8.11, 0.094, and 0.7, respectively.
[31]D. F. Mullica, H. O. Perkins, C. K. C. Lok, and V. Young, J. Electron Spectrosc. Relat. Phenom. **61**, 337 (1993).