October 2008
SLAC-PUB-13448

Synchrotron Radiation Photoemission Spectroscopic Study of Band Offsets and Interface Self-cleaning by Atomic Layer Deposited HfO_2 on $In_{0.53}Ga_{0.47}As$ and $In_{0.52}Al_{0.48}As$

M. Kobayashi[1], P. T. Chen[2], Y. Sun[3], N. Goel[4], P. Majhi[5], M Garner[4], W. Tsai[4], P. Pianetta[1,3] and Y. Nishi[1]

The Synchrotron Radiation Photoemission Spectroscopic (SRPES) study was conducted to (a) investigate the surface chemistry of $In_{0.53}Ga_{0.47}As$ and $In_{0.52}Al_{0.48}As$ post chemical and thermal treatments, (b) construct band diagram and (c) investigate the interface property of $HfO_2/In_{0.53}Ga_{0.47}As$ and $HfO_2/In_{0.52}Al_{0.48}As$. Dilute HCl and HF etch remove native oxides on $In_{0.53}Ga_{0.47}As$ and $In_{0.52}Al_{0.47}As$, whereas *in-situ* vacuum annealing removes surface arsenic pile-up. After the atomic layer deposition of HfO_2, native oxides were considerably reduced compared to that in as-received epi-layers, strongly suggesting the self-clean mechanism. Valence and conduction band offsets are measured to be 3.37±0.1eV, 1.80±0.3eV for $In_{0.53}Ga_{0.47}As$ and 3.00±0.1eV, 1.47±0.3eV for $In_{0.52}Al_{0.47}As$, respectively.

KEYWORDS: ALD, self-clean, SRPES, InGaAs, InAlAs, HfO_2

Published in the Applied Physcis Letters

Work supported in part by US Department of Energy contract DE-AC02-76SF00515

---

[1] *Department of Electrical Engineering, Stanford University, 420 Via Pallou Mall, Stanford, California 94305, USA*
[2] *Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, USA*
[3] *Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, Menlo Park, California 94305, USA*
[4] *Intel Corporation, Santa Clara, California 95052, USA*
[5] *Intel Asiignee at SEMATECH, 2706, Montopolis Drive, Austin, Texas 78741, USA*
*E-Mail: masaharu@stanford.edu

The ever increasing need for higher speed and lower power computing has pushed Si-based transistors to scale down to their limit. High mobility III-V compound semiconductors are being actively evaluated in research as one of the promising technology boosters which can enhance the metal-oxide-semiconductor field-effect-transistors (MOSFETs) performance not only by relying on scaling. Among III-V semiconductor substrates, InGaAs and InAlAs have been used as a channel and barrier layer material and embraced the advantages of higher electron mobility and moderate bandgap as compared to Si [1-3]. In order to sustain a better gate capacitance scalability for metal-oxide-semiconductor (MOS) device application, high-k dielectrics have been deposited onto the III-V semiconductor substrates, such as GaAs and InGaAs [2-12].

Compared to the elemental semiconductors such as Si and Ge, III-V semiconductors are likely to form extrinsic defects through surface antisite defects and high interface state density due to native oxide, which showed a strong relation to Fermi-level pinning at the interface [13,14]. In order to prevent defect formation and Fermi-level pinning, various surface passivation techniques such as Si or Ge passivation [9], sulfur passivation [12], Ga_2O_3 (Gd_2O_3) passivation [10] have been proposed and demonstrated. However, Si and Ge are incorporated as dopants in III-V semiconductor substrate and alter the doping profile. Moreover, Si, Ge, and Ga_2O_3 passivation layers thicken the high-k gate dielectric with low-k interfacial layers, decreasing the effective dielectric constant of the gate dielectric stack thus preventing oxide physical thickness scaling to a reasonable range. Sulfur passivation is not stable at high thermal budget process [12].

Recent studies have demonstrated native-oxide-free interface of atomic layer deposited (ALD) high-k dielectrics on GaAs and InGaAs [2-5,7,8], but the detailed interface analysis has not yet been reported. In this work, we studied the interface properties of $HfO_2/In_{0.53}Ga_{0.47}As$ and $HfO_2/In_{0.52}Al_{0.48}As$ stacks by using Synchrotron Radiation Photoemission Spectroscopy (SRPES) [11-12]. Bandoffsets at the interface of HfO_2/InGaAs and InAlAs were experimentally constructed. The self-cleaning mechanism during ALD HfO_2 deposition was investigated through surface and interface analysis of InGaAs and InAlAs.

The $In_{0.53}Ga_{0.47}As$ and $In_{0.52}Al_{0.48}As$ films were grown by MBE on (100) InP wafers. The wafers were transferred *ex-situ* to ALD chamber where HfO_2 (1 and 10nm) was deposited and followed by post deposition annealing at 520^{o}C in a nitrogen ambient.

SRPES has large advantages in terms of high energy resolution and surface sensitivity. By utilizing SRPES, valence band (VB) offset was extracted by reading difference between VB maximum of bulk substrate and HfO_2. Ga 3d and In 4d core level spectrum peaks were used as reference peak positions to align substrate and HfO_2 spectra as shown in Fig. 1 for InGaAs and InAlAs, respectively. The details of VB offset extraction by SRPES were described in our previous works [11, 12]. Figure 1 (a) and (d) show the aligned Ga 3d/In 4d and VB spectra for InGaAs and In 4d and VB spectra for InAlAs, respectively. From Fig. 1 (a) and (d), VB offset for InGaAs and InAlAs to HfO_2 were determined to be 3.37 ± 0.1eV and 3.00 ± 0.1eV, respectively,

The HfO_2 bandgap was extracted from oxygen energy loss spectra [11,12] as shown in Fig. 1 (b) and (e). The HfO_2 bandgap is estimated to be 5.93 ± 0.2eV on InGaAs and InAlAs, respectively.

Taking $In_{0.53}Ga_{0.47}As$ and $In_{0.52}Al_{0.48}As$ bandgap (0.77eV and 1.46eV), into account, the band diagram of HfO_2 on InGaAs and InAlAs were experimentally constructed based on SRPES results as shown in Fig. 1 (c) and (f). The conduction band (CB) offsets of 1.80 ± 0.3eV and 1.47 ± 0.3eV for InGaAs and InAlAs should minimize electron tunneling for NMOSFET applications. Figure 2 (a) and (b) show gate capacitance versus gate voltage (*C*-*V*) and gate current versus gate voltage (*I*-*V*) characteristics of 10nm-thick HfO_2/InGaAs gate stack. Gate current is well suppressed due to the sufficiently high conduction band offset.

In order to understand chemical and thermal property of the interfaces, we started from understanding the surface chemistry of bare InGaAs and InAlAs substrates with native oxides. All chemical treatments were done in the argon glove box which is connected to the load-lock chamber of the SRPES system. In the as-received InGaAs substrate, spectra of native GaO_x, InO_x, and AsO_x were shown in Fig. 3 (a) (i) – (ii). After a 9% HCl wet etching, GaO_x, InO_x and AsO_x were effectively etched away as shown in the left of Fig. 3 (a) (iii) – (iv). In turn, surface elemental As-As bonding appeared after AsO_x reduction. In order to remove remaining native oxide and elemental As, *in-situ* ultrahigh vacuum (UHV, base pressure is 10^{-9}Torr) annealing at 400^{o}C was conducted in SRPES chamber. As a result, all native oxides were completely removed as shown in Fig. 3 (a) (v) – (vi). This was confirmed by observing surface-shift of Ga and In peaks in Fig. 3 (a) (v) and (vi) which were reported previously in oxide-free surface [15,16]. In addition, elemental As was also completely desorbed as shown in Fig. 3 (a) (vi).

In the case of InAlAs substrates, almost similar results were obtained for In and As spectra as shown in Fig. 3 (b), except that for AlO_x. Although hydrophobic surface was confirmed after HF and HCl wet surface cleaning, AlO_x was still detected which suggested the surface Al was immediately oxidized by residual oxygen in argon glove box after wet chemical treatment or through the distilled water. After UHV annealing, more AlO_x was grown as shown in Fig. 3 (b) (vii) possibly due to the oxygen transfer from the other oxide [17]. InO_x is likely to be the candidate because of the low formation free energy of Al_2O_3 (The standard formation free energy (kJ/mol: As_2O_3 –782.3, Ga_2O_3 –998.3, In_2O_3 –830.7 and Al_2O_3 –1582.3) [18].

To remove native AlO_x, we also applied HF wet surface cleaning with different concentration and dipping time (1% or 10%, 1min or 10mins). From SRPES experiment, it was confirmed that although HF can etch more AlO_x than HCl, AlO_x still cannot be completely removed.

ALD HfO_2 was grown on the as-received InGaAs and InAlAs substrates where the native oxides were intentionally left in order to examine the transition of native oxides before and after ALD process. No wet surface cleaning was conducted prior to ALD HfO_2 deposition. In order to expose the interface, step-by-step wet etch-back of 10nm-thick HfO_2 was conducted by using dilute HF and carefully monitoring surface spectra [12]. Fig. 4 (a) and (b) shows the etch-back profile of HfO_2 on InGaAs and InAlAs. After 55 and 57sec etch, Ga 3d and In 4d peak feature appeared in HfO_2/InGaAs and HfO_2/InAlAs stack, respectively. It should be noted that very thin HfO_2 was left in order not to etch the interfacial layer by dilute HF. Once the substrate peaks are detected, the interface was scanned by SRPES.

At the interface of HfO_2/InGaAs, the amount of native GaO_x, InO_x and AsO_x appear to be significantly reduced from the initial as-received substrates and surface elemental As-As bonding appears, as shown in Fig. 3 (a) (i) – (iii) with Fig. 4 (c). This result is analogous to HCl or HF wet chemical clean as shown in the surface analysis in Fig. 3 (a) (iv) – (vi). This demonstrates the self-cleaning process during ALD HfO_2 deposition and its highly reactive chemical reaction. Similar results were seen in the HfO_2/InAlAs stack as shown in Fig. 3 (b) (i) – (iii) and 4 (d). Native oxides including AlO_x were clearly reduced from the initial amount of native oxides.

Figure 5 (a) and (b) show the cross section transmission electron microscopy (TEM) image of native oxides/InGaAs substrate and HfO_2/InGaAs stack, respectively. The thickness of the native oxide was estimated to be 2nm and was reduced down to less than 1nm after ALD HfO_2 deposition. In Fig. 5 (c) and (d), the electron energy loss spectra (EELS) show composition profiles of the InGaAs substrate with native oxide and HfO_2/InGaAs gate stack, respectively. The native oxide were significantly reduced after the ALD HfO_2 deposition.

In conclusions, band offsets and bandgaps of HfO_2/InGaAs and HfO_2/InAlAs stacks were experimentally obtained from SRPES spectra: $\Delta E_c = 1.80 \pm 0.3$eV and 1.47 ± 0.3eV for HfO_2/InGaAs and HfO_2/InAlAs, respectively. The sufficient conduction band offsets revealed that these stacks are scalable in terms of gate leakage for NMOSFET applications. The surface chemistry of InGaAs and InAlAs was examined by HCl and HF wet chemical treatment and *in-situ* high vacuum annealing. In both InGaAs and InAlAs, HCl wet clean removed native oxides and formed surface elemental As. By in-situ annealing, native oxides and surface elemental As were desorbed. The interface of HfO_2/InGaAs and HfO_2/InAlAs were also investigated by using etch-back experiments. After the ALD deposition, native oxides are evidently reduced from the initial as-received substrates.

Portions of this research were carried out at the Stanford Synchrotron Radiation Laboratory, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences. The authors acknowledge Intel for financial support. The authors also acknowledge C. K. Gaspe and M. B. Santos in University Oklahoma for MBE growth of samples and S. Koveshnikov (Intel) for technical help.

References

[1] D. –H. Kim, J. A. del Alamo, J. –H. Lee, and K. –S. Seo, Int. Electron Devices Meet. **2005**, 767

[2] 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)

[3] M. K. Hudait, G. Dewey, S. Datta, J. M. Fastenau, J. Kavalieros, W. K. Liu, D. Lubyshev, R. Pillarisetty, W. Rachmady, M. Radosavljevic, T. Rakshit and R. Chau, Tech. Dig. – Int. Electron Devices Meet. 2007, 625

[4] C. –H. Chang, Y. –K. Chiou, Y. –C. Chang, K. –Y. Lee, T. –D. Lin, T.-B. Wu, and M. Hong, Appl. Phys. Lett., **89** 242911 (2006)

[5] N. Goel, P. Majhi, C. O. Chui, W. Tsai, D. Choi, and J. S. Harris, Appl. Phys. Lett., **89** 163517 (2006)

[6] S. Oktyabrsky, S. Oktyabrsky V. Tokranov, M. Yakimov, R. Moore, S. Koveshnikov, W. Tsai, F. Zhu and J.C. Lee, Mat. Sci. Engineer. B **135** 272 (2006)

[7] 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)

[8] 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)

[9] H. –S. Kim, I. Ok, M. Zhang, T. Lee, F. Zhu, L. Yu and J. C. Lee, Appl. Phys. Lett., 89 222903 (2006)

[10] M. Passlack, M. Hong and J. P. Mannaerts, Appl. Phys. Lett., 68 1099 (1996)

[11] N. Goel, W. Tsai, C. M. Garner, Y. Sun, P. Pianetta, M. Warusawithana, D. G. Schlom, H. Wen, C.

Gaspe, J. C. Keay, M. B. Santos, L. V. Goncharova, E. Garfunkel, and T. Gustafsson, Appl. Phys. Lett., **91** 118515 (2007)

[12] P. T. Chen, Y. Sun, E. Kim, P. C. McIntyre, W. Tsai, M. Garner, P. Pianetta, Y. Nishi, and C. O. Chui, J. Appl. Phys., **103** 034106 (2008)

[13] W. E. Spicer, Z. L. 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)

[14] M. J. Hale, S. I. Yi, J. Z. Sexton, A. C. Kummel, M. Passlack, J. Appl. Phys., **119** 6719 (2003)

[15] Z. Liu, Y. Sun, F. Machuca, P. Pianetta, W. E. Spicer, and R. F. W. Pease, J. Vac. Sci. Technol. A **21** 212 (2003)

[16] Y. Sun, Z. Liu, F. Machuca, P. Pianetta, and W. E. Spicer, J. Vac. Sci. Technol. A **21** 219 (2003)

[17] S. I. J. Ingrey, W. M. Lau, and R. N. S. Sodhi, J. Vac. Sci. Technol. A **7** 1554 (1989)

[18] CRC “*Handbook of Chemistry and Physics*”, 88th Edition (2007)

Figure captions

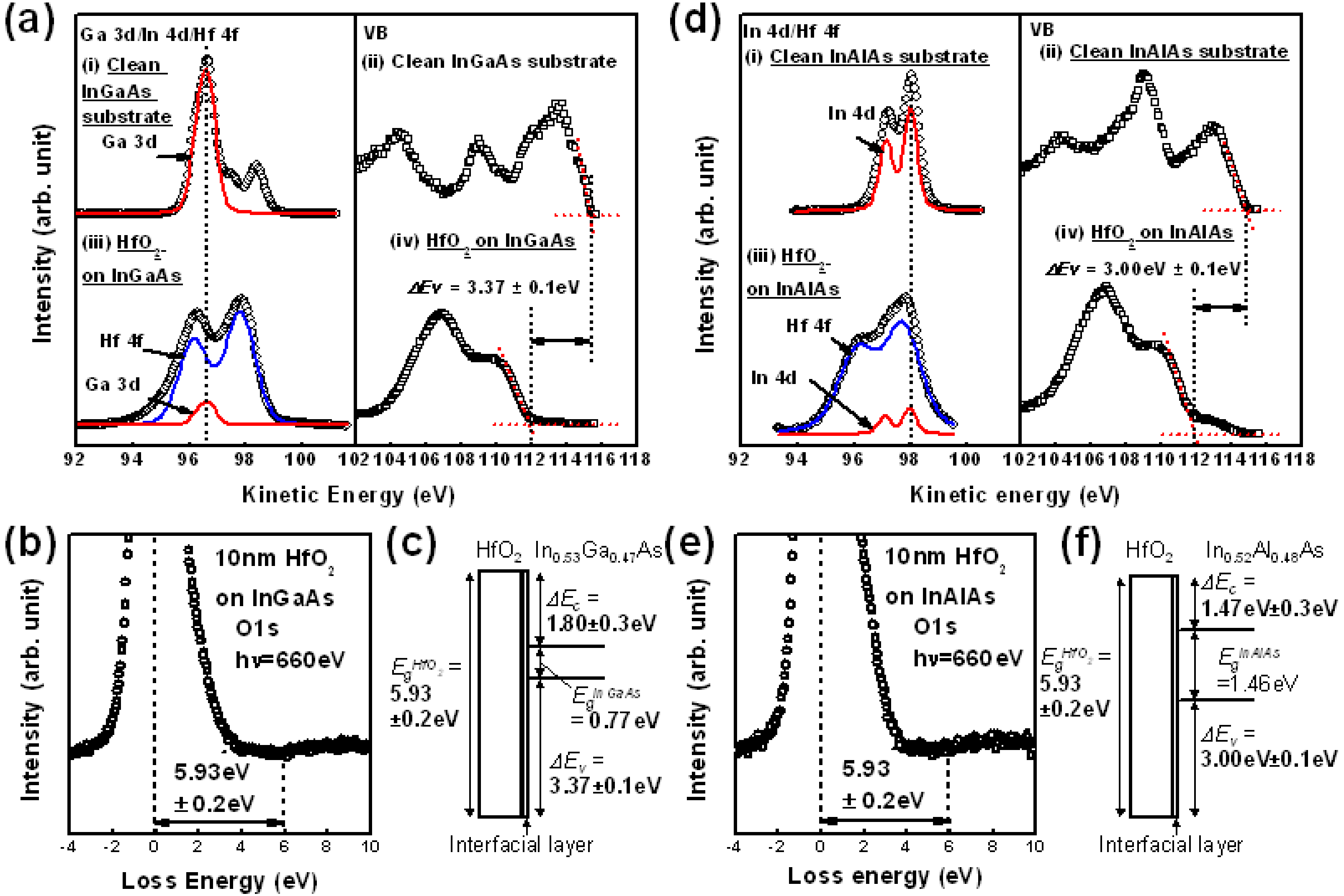
Figure 1 (a) (i) Ga 3d/In 4d/Hf 4f spectra and (ii) valence band (VB) spectrum of the clean InGaAs substrate. (iii) Ga 3d/In 4d/Hf 4f spectra and (iv) VB spectrum of HfO_2 on InGaAs substrates. VB offset is 3.37 ± 0.1eV. (b) O 1s energy loss spectrum of HfO_2 on InGaAs. HfO_2 bandgap is 5.93 ± 0.2eV. (c) The band diagram of HfO_2/InGaAs. Conduction band (CB) offset is 1.80 ± 0.3eV. (d) (i) In 4d/Hf 4f spectra and (ii) VB spectrum of the clean InAlAs substrate. (iii) In 4d/Hf 4f spectra and (iv) VB spectrum of HfO_2 on InAlAs substrates. VB offset is 3.37 ± 0.1eV. (e) O 1s energy loss spectrum of HfO_2 on InAlAs. HfO_2 bandgap is 5.93 ± 0.2eV. (f) The band diagram of HfO_2. CB offset is 1.47 ± 0.3eV.

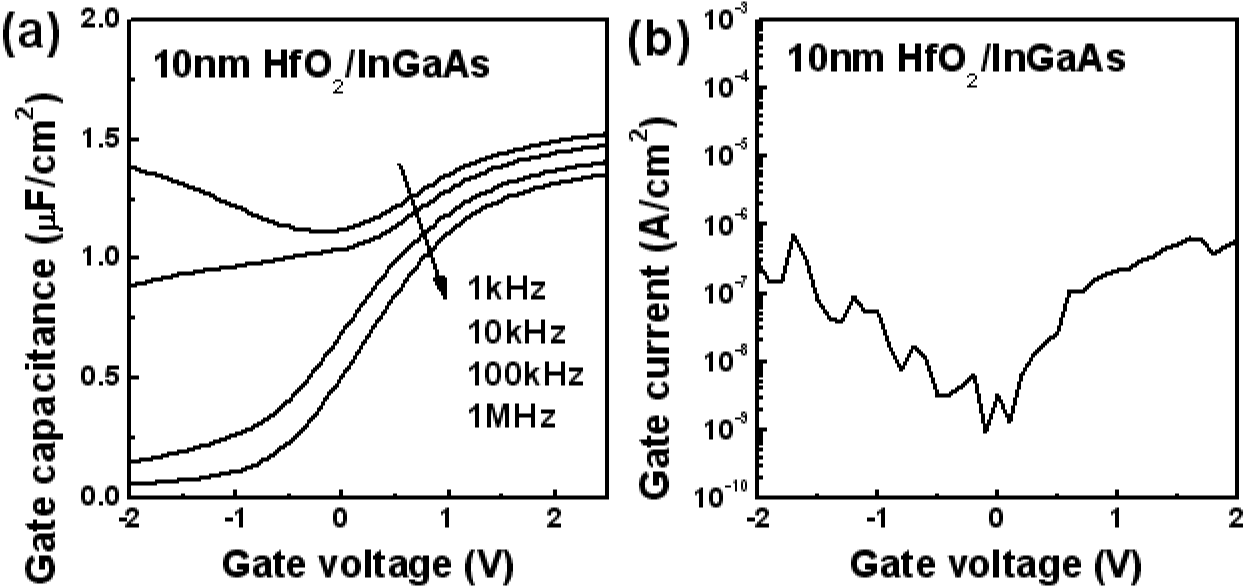
Figure 2 (a) Measured gate capacitance versus gate voltage characteristics and (b) Measured gate current versus gate voltage characteristics of 10nm-thick HfO_2/n-InGaAs gate stack, respectively.

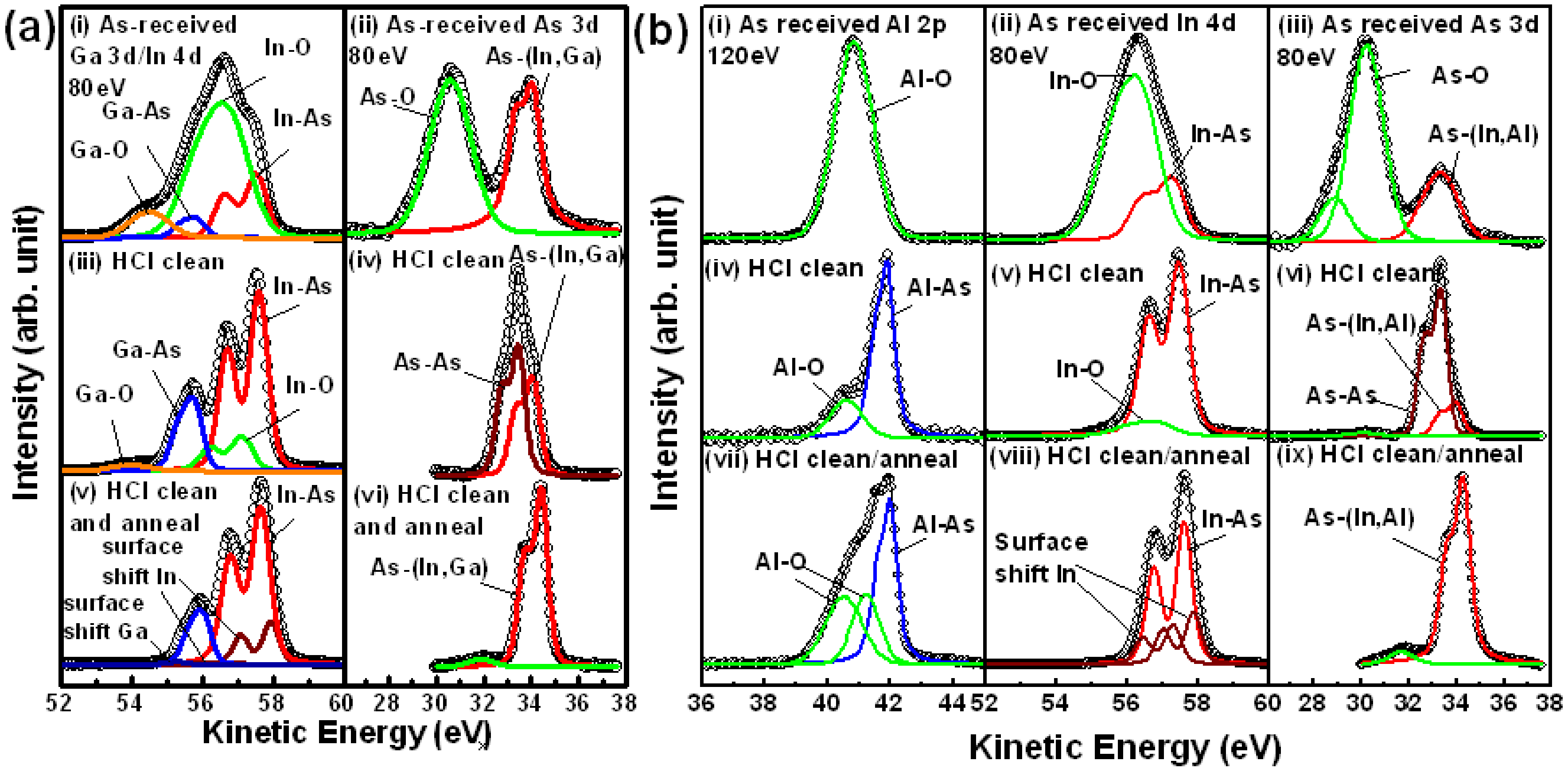
Figure 3 (a) Ga 3d/In 4d and As 3d spectra of InGaAs surface with different treatment: (i) (ii) as-received sample, (iii) (iv) HCl wet surface cleaning, (v) (vi) HCl wet surface cleaning and *in-situ* high vacuum chamber annealing at 400^{o}C. (b) Al 2p, In 4d and As 3d spectra of InAlAs surface with different treatment: (i) (ii) as-received sample, (iii) (iv) HCl wet surface cleaning, (v) (vi) HCl wet surface cleaning and *in-situ* high vacuum chamber annealing at 400^{o}C

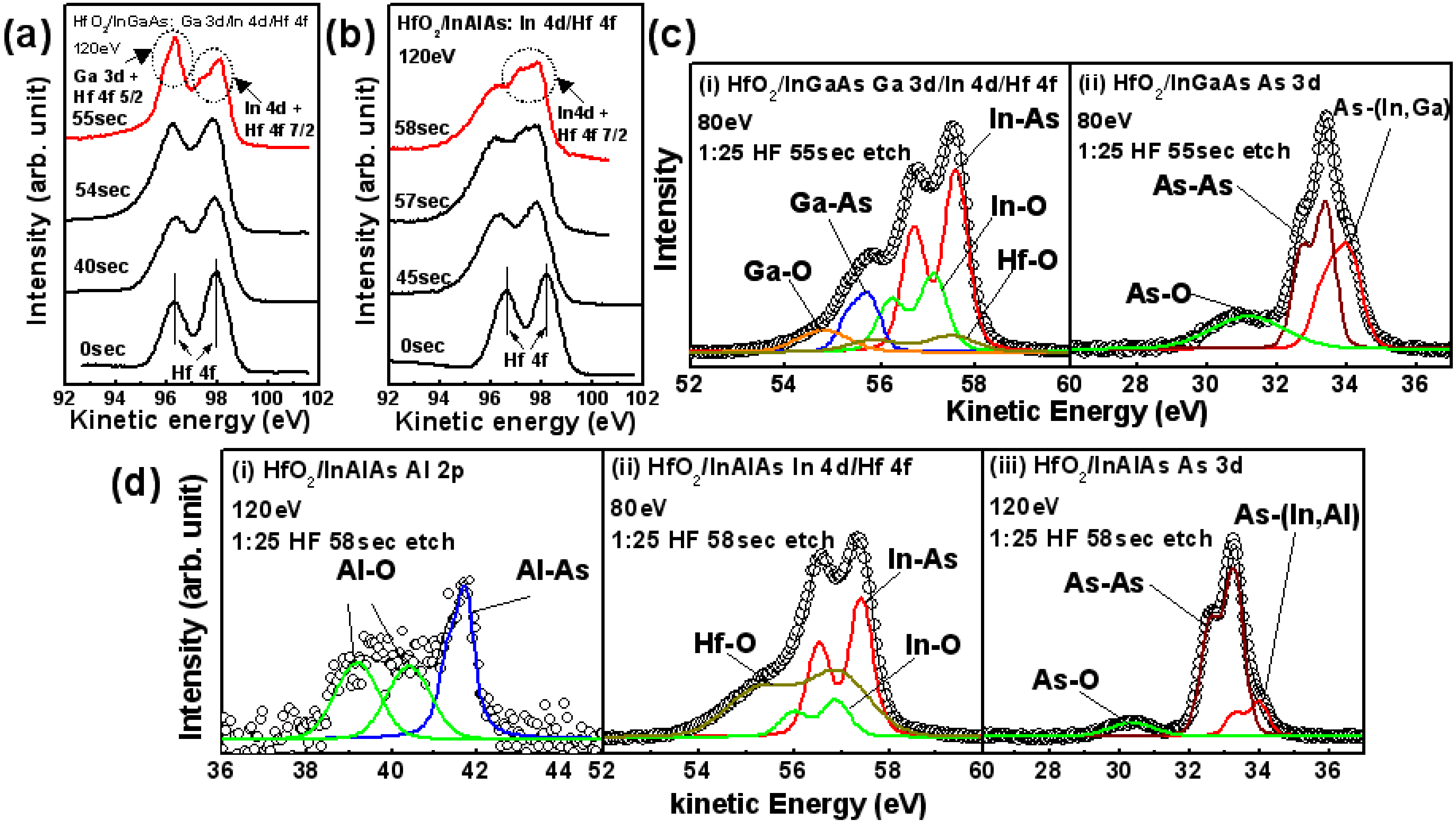
Figure 4 (a) HfO_2 etch back profile on InGaAs. Ga 3d peak feature was detected after 55sec HF etch. (b) HfO_2 etch back profile on InAlAs. In 4d peak feature was detected after 57sec dilute HF etch. (c) Ga 3d/In 4d/Hf 4f and As 3d spectra of the interface of HfO_2 and InGaAs. (d) Al 2p, In 4d/Hf 4f and As 3d spectra of the interface of HfO_2 and InAlAs.

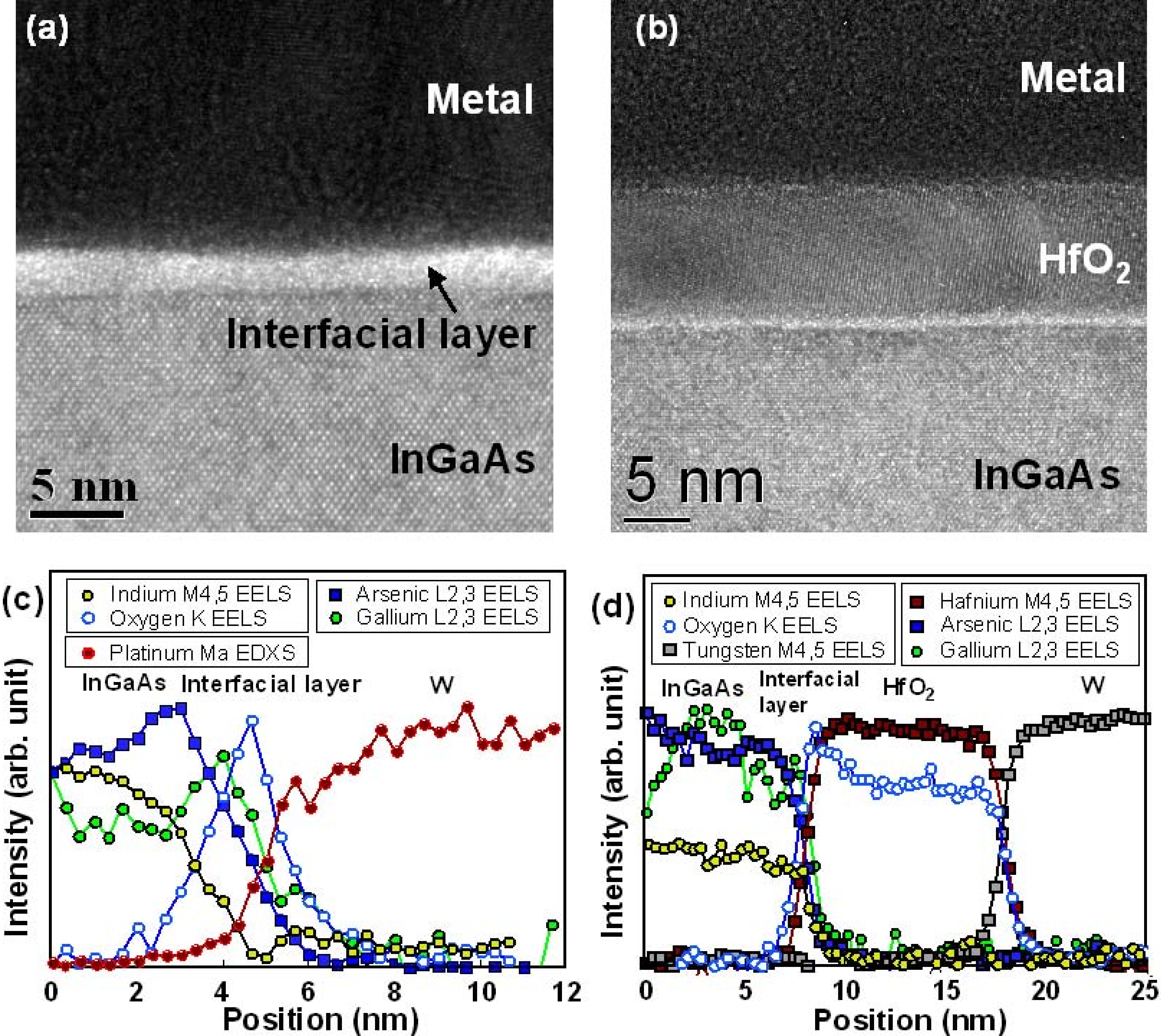
Figure 5 (a) (b) Cross sectional TEM image of as-received InGaAs substrate with native oxide capped with a metal and W/HfO_2/InGaAs, respectively. It should be noted that HfO_2 was directly deposited on InGaAs with the native oxides. The native oxide thickness was reduced from 2nm to less than 1nm after ALD HfO_2 deposition. (c) (d) Cross sectional composition information measured by electron energy loss spectroscopy (EELS) of as-received InGaAs substrate with native oxide and W/HfO_2/InGaAs, respectively.


(a)
Ga 3d/In 4d/Hf 4f
(i) Clean InGaAs substrate
Ga 3d
(iii) HfO2- on InGaAs
Hf 4f
Ga 3d
VB
(ii) Clean InGaAs substrate
(iv) HfO2 on InGaAs
ΔEv = 3.37 ± 0.1eV
Intensity (arb. unit)
92 94 96 98 100 102 104 106 108 110 112 114 116 118
Kinetic Energy (eV)
(d)
In 4d/Hf 4f
(i) Clean InAlAs substrate
In 4d
(iii) HfO2- on InAlAs
Hf 4f
In 4d
VB
(ii) Clean InAlAs substrate
(iv) HfO2 on InAlAs
ΔEv = 3.00eV ± 0.1eV
Intensity (arb. unit)
92 94 96 98 100 102 104 106 108 110 112 114 116 118
Kinetic energy (eV)
(b)
10nm HfO2 on InGaAs
O1s
hν=660eV
5.93eV ±0.2eV
Intensity (arb. unit)
-4 -2 0 2 4 6 8 10
Loss Energy (eV)
(c)
HfO2
In0.53Ga0.47As
ΔEc = 1.80±0.3eV
Eg HfO2 = 5.93 ±0.2eV
Eg InGaAs = 0.77 eV
ΔEv = 3.37±0.1eV
Interfacial layer
(e)
10nm HfO2 on InAlAs
O1s
hν=660 eV
5.93 ± 0.2eV
Intensity (arb. unit)
-4 -2 0 2 4 6 8 10
Loss energy (eV)
(f)
HfO2
In0.52Al0.48As
ΔEc = 1.47eV±0.3eV
Eg HfO2 = 5.93 ±0.2eV
Eg InAlAs =1.46 eV
ΔEv = 3.00eV±0.1eV
Interfacial layer


(a)
10nm HfO2/InGaAs
Gate capacitance (μF/cm2)
2.0
1.5
1.0
0.5
0.0
1kHz
10kHz
100kHz
1MHz
-2
-1
0
1
2
Gate voltage (V)
(b)
10nm HfO2/InGaAs
Gate current (A/cm2)
10-3
10-4
10-5
10-6
10-7
10-8
10-9
10-10
-2
-1
0
1
2
Gate voltage (V)


(a)
(i) As-received Ga 3d/In 4d 80 eV
In-O
Ga-As
In-As
Ga-O
(ii) As-received As 3d 80 eV
As-(In,Ga)
As-O
(iii) HCl clean
In-As
Ga-As
In-O
Ga-O
(iv) HCl clean
As-(In,Ga)
As-As
(v) HCl clean and anneal
In-As
surface shift In
surface shift Ga
(vi) HCl clean and anneal
As-(In,Ga)
Intensity (arb. unit)
52
54
56
58
60
28
30
32
34
36
38
Kinetic Energy (eV)
(b)
(i) As received Al 2p 120eV
Al-O
(ii) As received In 4d 80eV
In-O
In-As
(iii) As received As 3d 80eV
As-O
As-(In,Al)
(iv) HCl clean
Al-As
Al-O
(v) HCl clean
In-As
In-O
(vi) HCl clean
As-(In,Al)
As-As
(vii) HCl clean/anneal
Al-As
Al-O
(viii) HCl clean/anneal
Surface shift In
In-As
(ix) HCl clean/anneal
As-(In,Al)
Intensity (arb. unit)
36
38
40
42
44
52
54
56
58
60
28
30
32
34
36
38
Kinetic Energy (eV)


(a)
HfO$_2$/InGaAs: Ga 3d/In 4d/Hf 4f
120eV
Ga 3d + Hf 4f 5/2
In 4d + Hf 4f 7/2
55sec
54sec
40sec
0sec
Hf 4f
Intensity (arb. unit)
Kinetic energy (eV)
92 94 96 98 100 102
(b)
HfO$_2$/InAlAs: In 4d/Hf 4f
120eV
In4d + Hf 4f 7/2
58sec
57sec
45sec
0sec
Hf 4f
Intensity (arb. unit)
Kinetic energy (eV)
92 94 96 98 100 102
(c)
(i) HfO$_2$/InGaAs Ga 3d/In 4d/Hf 4f
80eV
1:25 HF 55sec etch
In-As
Ga-As
In-O
Hf-O
Ga-O
(ii) HfO$_2$/InGaAs As 3d
80eV
1:25 HF 55sec etch
As-(In,Ga)
As-As
As-O
Intensity
52 54 56 58 60 28 30 32 34 36
Kinetic Energy (eV)
(d)
(i) HfO$_2$/InAlAs Al 2p
120eV
1:25 HF 58sec etch
Al-O
Al-As
(ii) HfO$_2$/InAlAs In 4d/Hf 4f
80eV
1:25 HF 58sec etch
In-As
Hf-O
In-O
(iii) HfO$_2$/InAlAs As 3d
120eV
1:25 HF 58sec etch
As-(In,Al)
As-As
As-O
Intensity (arb. unit)
36 38 40 42 44 52 54 56 58 60 28 30 32 34 36
kinetic Energy (eV)


(a)
Metal
Interfacial layer
InGaAs
5 nm
(b)
Metal
HfO_2
InGaAs
5 nm
(c)
Indium M4,5 EELS
Oxygen K EELS
Arsenic L2,3 EELS
Gallium L2,3 EELS
Platinum Ma EDXS
InGaAs
Interfacial layer
W
Intensity (arb. unit)
0
2
4
6
8
10
12
Position (nm)
(d)
Indium M4,5 EELS
Oxygen K EELS
Tungsten M4,5 EELS
Hafnium M4,5 EELS
Arsenic L2,3 EELS
Gallium L2,3 EELS
InGaAs
Interfacial layer
HfO_2
W
Intensity (arb. unit)
0
5
10
15
20
25
Position (nm)