

Synchrotron Radiation Photoemission Spectroscopic Study of Band Offsets and Interface Self-cleaning by Atomic Layer Deposited HfO₂ on In_{0.53}Ga_{0.47}As and In_{0.52}Al_{0.48}As

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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 HfO₂/In_{0.53}Ga_{0.47}As and HfO₂/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 HfO₂, 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, HfO₂

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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 $\text{HfO}_2/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ and $\text{HfO}_2/\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ stacks by using Synchrotron Radiation Photoemission Spectroscopy (SRPES) [11-12]. Bandoffsets at the interface of $\text{HfO}_2/\text{InGaAs}$ 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 $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ and $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ 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°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 $3.37 \pm 0.1\text{eV}$ and $3.00 \pm 0.1\text{eV}$, 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 $5.93 \pm 0.2\text{eV}$ on InGaAs and InAlAs , respectively.

Taking $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ and $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ 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 $1.80 \pm 0.3\text{eV}$ and $1.47 \pm 0.3\text{eV}$ 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 $\text{HfO}_2/\text{InGaAs}$ 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°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 $\text{HfO}_2/\text{InGaAs}$ and $\text{HfO}_2/\text{InAlAs}$ 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 $\text{HfO}_2/\text{InGaAs}$, 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 HfO₂ deposition and its highly reactive chemical reaction. Similar results were seen in the HfO₂/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 HfO₂/InGaAs stack, respectively. The thickness of the native oxide was estimated to be 2nm and was reduced down to less than 1nm after ALD HfO₂ deposition. In Fig. 5 (c) and (d), the electron energy loss spectra (EELS) show composition profiles of the InGaAs substrate with native oxide and HfO₂/InGaAs gate stack, respectively. The native oxide were significantly reduced after the ALD HfO₂ deposition.

In conclusions, band offsets and bandgaps of HfO₂/InGaAs and HfO₂/InAlAs stacks were experimentally obtained from SRPES spectra: $\Delta E_c = 1.80 \pm 0.3\text{eV}$ and $1.47 \pm 0.3\text{eV}$ for HfO₂/InGaAs and HfO₂/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 HfO₂/InGaAs and HfO₂/InAlAs

were also investigated by using etch-back experiments. After the ALD deposition, native oxides are evidently reduced from the initial as-received substrates.

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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 HfO₂ on InGaAs substrates. VB offset is $3.37 \pm 0.1\text{eV}$. (b) O 1s energy loss spectrum of HfO₂ on InGaAs. HfO₂ bandgap is $5.93 \pm 0.2\text{eV}$. (c) The band diagram of HfO₂/InGaAs. Conduction band (CB) offset is $1.80 \pm 0.3\text{eV}$. (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 HfO₂ on InAlAs substrates. VB offset is $3.37 \pm 0.1\text{eV}$. (e) O 1s energy loss spectrum of HfO₂ on InAlAs. HfO₂ bandgap is $5.93 \pm 0.2\text{eV}$. (f) The band diagram of HfO₂. CB offset is $1.47 \pm 0.3\text{eV}$.

Figure 2 (a) Measured gate capacitance versus gate voltage characteristics and (b) Measured gate current versus gate voltage characteristics of 10nm-thick HfO₂/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°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°C

Figure 4 (a) HfO₂ etch back profile on InGaAs. Ga 3d peak feature was detected after 55sec HF etch. (b) HfO₂ 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 HfO₂ and InGaAs. (d) Al 2p, In 4d/Hf 4f and As 3d spectra of the interface of HfO₂ and InAlAs.

Figure 5 (a) (b) Cross sectional TEM image of as-received InGaAs substrate with native oxide capped with a metal and W/HfO₂/InGaAs, respectively. It should be noted that HfO₂ was directly deposited on InGaAs with the native oxides. The native oxide thickness was reduced from 2nm to less than 1nm after ALD HfO₂ deposition. (c) (d) Cross sectional composition information measured by electron energy loss spectroscopy (EELS) of as-received InGaAs substrate with native oxide and W/HfO₂/InGaAs, respectively.









