

Synchrotron Radiation Photoemission Spectroscopic Study of Band Offsets and Interfacial Self-cleaning Mechanism in Atomic Layer Deposited HfO₂ on InGaAs and InAlAs

M. Kobayashi¹, P. T. Chen¹, S. Sun², N. Goel³, M. Garner³, W. Tsai³, P. Pianetta² and Y. Nishi¹

¹Department of Electrical Engineering, Stanford University, 420 Via Pallou Mall, Stanford, CA, E-mail: masaharu@stanford.edu

²Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, ³Intel Corporation

Introduction

Si-based transistors are constantly scaled down to their limit for the ever increasing need for higher speed and lower power computing. High mobility III-V compound semiconductors are being actively evaluated in research as one of the promising technology boosters which can enhance the device performance not only by relying on scaling. InGaAs and InAlAs are used as a channel and barrier layer material and embrace the advantages of higher electron mobility and larger bandgap as compared to Si [1,2]. In order to sustain a better gate capacitance scalability for metal-oxide-semiconductor (MOS) device application, high-k dielectrics has been deposited onto the InGaAs substrates [2-5]. Recent study demonstrated native-oxide-free interface of high-k dielectrics/GaAs and InGaAs gate stack possibly because of self-cleaning during Atomic-Layer-Deposition (ALD) process [2-7]. Comparing to elemental semiconductors such as Si and Ge, III-V semiconductors are likely to form defects which cause Fermi-level pinning at the interface by extrinsic defects such as surface antisite defects and high interface state density due to native oxide [8,9]. Although it is important to understand the interface property of HfO₂/InGaAs and HfO₂/InAlAs, however, the detail interface analysis has not adequately been done yet. In this work, we studied the interface property of HfO₂/InGaAs and HfO₂/InAlAs stacks by using Synchrotron Radiation Photoemission Spectroscopy (SRPES) [10-13]. Bandoffsets at the interface of HfO₂/InGaAs and InAlAs were constructed. Then, self-cleaning mechanism during ALD HfO₂ deposition was investigated through surface and interface analysis of InGaAs and InAlAs.

Band offset extraction

The In_{0.53}Ga_{0.47}As and In_{0.52}Al_{0.48}As films were grown by MBE on semi-insulating (100) InP wafers. Then 10nm-thick HfO₂ layers were deposited on the wafers by Atomic Layer Deposition (ALD) system by *ex-situ*.

Since SRPES has a high energy resolution at the valence band (VB) spectrum maximum, valence band offset can be precisely extracted by taking difference between VB maximum of bulk substrate and HfO₂. Ga 3d and In 4d spectrum peaks were used as a reference. In order to thin the HfO₂ layer to a thickness that allows detection of Ga and In core levels, HfO₂ etch-back was done by diluted HF solution as shown in Fig. 1 and 3. Reference Ga and In peaks clearly appeared at 55 and 58 sec for InGaAs and InAlAs, respectively. VB offset for InGaAs and InAlAs to HfO₂ were determined to be 3.37eV and 3.00eV, respectively, as illustrated in Fig. 2 and 4.

The HfO₂ bandgap was extracted from oxygen energy loss spectrum [10,11] as shown in Fig. 5 and 7. The HfO₂ bandgap is estimated 5.94eV and 5.93eV on InGaAs and InAlAs.

Finally, taking InGaAs and InAlAs bandgap, 0.77eV and 1.46eV, into account, the band diagram of HfO₂ on InGaAs and InAlAs were constructed based on SRPES results as shown in Fig. 6 and 8. The conduction band (CB) offsets of 1.80eV and 1.47eV for InGaAs and InAlAs should minimize electron tunneling for NMOSFET applications, which is consistent with our previous electrical characterization [6].

Surface analysis of InGaAs and InAlAs

In order to understand chemical and thermal property of the interfaces, we started from the surface analysis of bare InGaAs and InAlAs substrates with native oxides. In as-received InGaAs substrates, native GaO_x, InO_x, and AsO_x were grown as shown in Fig. 9 (a) and (b). HCl is known as an acid which effectively etches native oxide. After 9% HCl etching, although GaO_x and InO_x still remained, however AsO_x were completely etched away as shown in Fig 9 (c) and (d). In turn, surface elemental As appeared because As precipitates are formed after AsO_x removal. In order to

remove remaining native oxide and elemental As, *in-situ* ultrahigh vacuum (UHV) annealing at 400°C was conducted. As a result, GaO_x and InO_x were completely removed. This was confirmed by observing surface-shift Ga and In peak in Fig. 9 (e) [12,13]. In addition, elemental As was also completely removed by As desorption in Fig. 9(f). In the case of InAlAs substrates, almost the same results were obtained except native AlO_x still remained even after HCl etching and annealing as shown in Fig. G (d) and (g). After annealing, more Al-suboxide was grown by possible transfer of oxygen from other oxide [14] with InO_x being a likely candidate because of the low formation free energy of AlO_x as shown in Table 1 [15].

Interface analysis of HfO₂/InGaAs and InAlAs

ALD HfO₂ was grown on the as-received InGaAs and InAlAs substrates which have native oxides in order to examine the transition of native oxides before and after ALD process. In order to expose the interface, step-by-step wet etch back was conducted by diluted HF as described earlier. At the interface of HfO₂/InGaAs, it was seen that the amount of native GaO_x, InO_x and AsO_x were significantly reduced from the initial as-received substrates by comparing Fig. 11 (a), (b) and Fig. 9 (a), (b). Fig. 12 shows the intensity ratio of oxide bonding to substrate bonding peak. Oxide species after ALD processing are clearly reduced from the initial substrates. This result resembles HCl wet clean result in the surface analysis. HCl solution reduces the native oxides to elements so that surface elemental As appears. This result is therefore probably due to the self-cleaning process during ALD HfO₂ deposition and its highly reactive chemical reaction. The possible model can be proposed: Hf precursor reacts with native oxide, most likely AsO_x with high formation free energy, Hf is oxidized to HfO₂, and then native oxide is reduced to elements as illustrated in Fig. 15. As a proof, elemental As which was not observed on the initial substrate was clearly observed at the interface. This As may form As antisite defect on missing Ga site and cause large density of gap state and Fermi-level pinning [8, 9]. GaO_x and InO_x will also be reduced and they may form InGaAs rather than elemental precipitates. The same phenomenon was seen in the HfO₂/InAlAs stack as shown in Fig. 12 and 13, except the large amount of AlO_x still remains which may degrade interface property in high-k/InAlAs gate stack.

Summary

The SRPES study constructed band diagram of HfO₂/InGaAs and HfO₂/InAlAs stacks and revealed that these stacks are scalable in terms of conduction band offset for NMOSFET application. The surface of InGaAs and InAlAs was analyzed. In both InGaAs and InAlAs, HCl wet clean generated surface elemental As. By *in-situ* annealing, native oxides and also surface elemental As was completely removed. The interface of HfO₂/InGaAs and HfO₂/InAlAs was also investigated by using etch-back experiments. After the ALD deposition, native oxides are clearly reduced from the initial as-received substrates. ALD deposition process with highly reactive Hf precursor can self-clean the III-V semiconductor surface and provide oxide-free interface.

Acknowledgement

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Reference

- [1] D. -H. Kim et al., IEDM Tech. Dig. 767 (2005) [2] P. D. Ye et al., APL 84 434 (2004) [3] C. -H. Chang et al., APL 89 242911 (2006) [4] N. Goel et al., APL 89 163517 (2006) [5] S. Oktyabrsky et al., Mat. Sci. Engineer. B 135 272 (2006) [6] M. L. Huang et al., APL 87 252104 (2005) [7] M. M. Frank et al., APL 86 152904 (2005) [8] N. Goel et al., APL 91 118515 (2007) [9] W. E. Spicer et al., J. Vac. Sci. Technol. B 6 1245 (1988) [10] M. J. Hale et al., JAP 119 6719 (2003) [11] N. Goel et al., APL 91 113515 (2007) [12] P. T. Chen et al., JAP 103 034106 (2008) [13] Z. Liu et al., J. Vac. Sci. Technol. A 21 212 (2003) [14] Y. Sun et al., J. Vac. Sci. Technol. A 21 219 (2003) [15] S. I. J. Ingrej et al., J. Vac. Sci. Technol. A (3) 1554 (1989) [16] K. Eguchi et al., JJAP 24 1043 (1985)

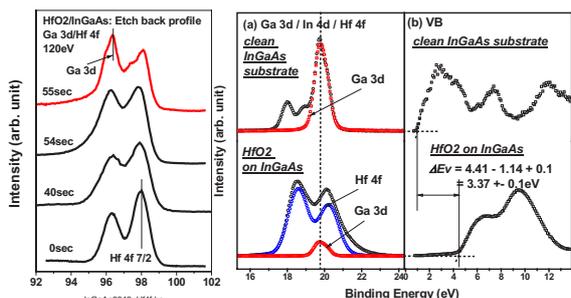


Fig. 1 Etch-back profile of Ga 3d/In 4d/Hf 4f spectrum of HfO₂/InGaAs. (a) Ga 3d/In 4d/Hf 4f spectrum after and before etch-back. (b) VB spectrum after and before etch-back.

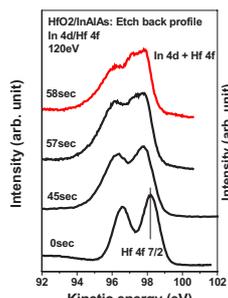


Fig. 3 Etch-back profile of Ga 3d/In 4f spectrum of HfO₂/InGaAs. (a) In 4d/Hf 4f spectrum after and before etch-back. (b) VB spectrum after and before etch-back.

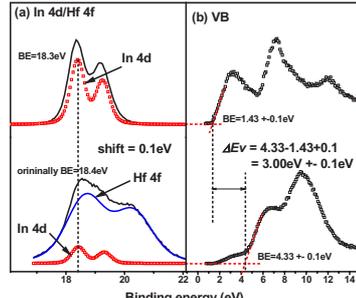


Fig. 4 (a) In 4d/Hf 4f spectrum after and before etch-back. (b) VB spectrum after and before etch-back.

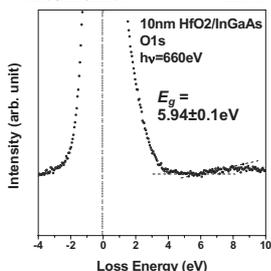


Fig. 5 Oxygen 1s energy loss spectrum of HfO₂/InGaAs.

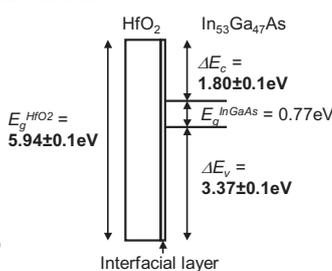


Fig. 6 Experimentally constructed Energy band diagram of HfO₂/InGaAs.

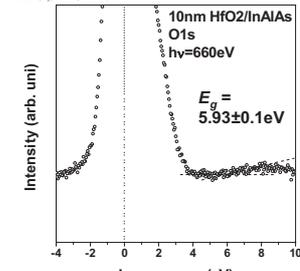


Fig. 7 Oxygen 1s energy loss spectrum of HfO₂/InAlAs.

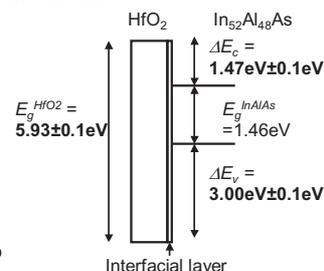


Fig. 8 Experimentally constructed energy band diagram of HfO₂/InGaAs

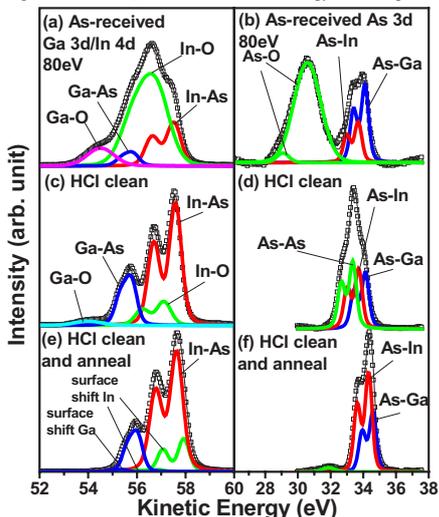


Fig. 9 Ga 3d/In 4d and As 3d spectrum of (a, b) as-received, (c, d) HCl clean, (e, f), HCl clean + annealed, InGaAs

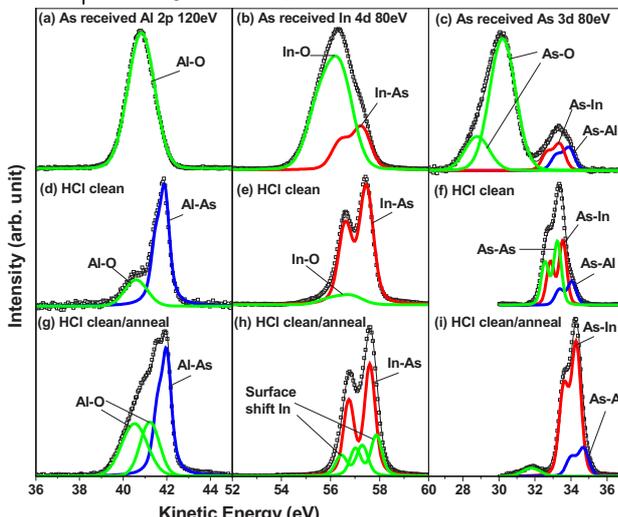


Fig. 10 Al 2p, In 4d and As 3d spectrum of (a, b, c) as-received, (d, e, f) HCl clean, (g, h, i) HCl clean + annealed, InAlAs substrate.

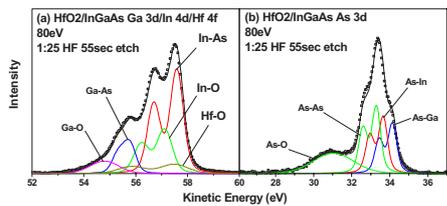


Fig. 11 (a) Ga 3d/In 4d/Hf 4f spectrum at the interface of HfO₂/InGaAs after 55sec etch-back.

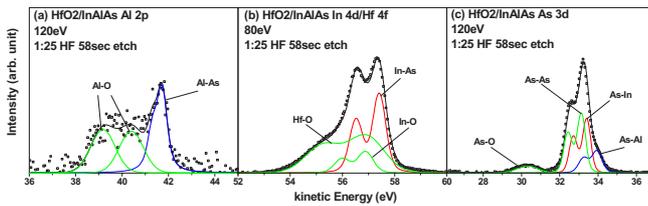


Fig. 12 (a) Al 2p, In 4d/Hf 4f and As 3d spectrum at the interface of HfO₂/InAlAs after 58sec etch-back.

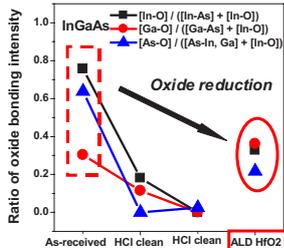


Fig. 13 The Ratio of oxide bonding intensity to substrate intensity with different treatment.

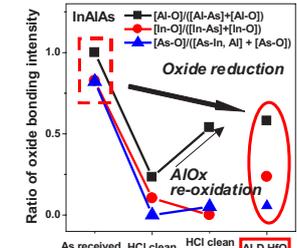


Fig. 14 The ratio of oxide bonding intensity to substrate intensity with different treatment.

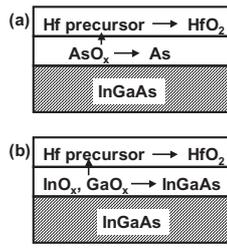


Fig. 15 The schematic of self clean mechanism in the case of HfO₂ deposition on InGaAs

Table 1 Standard formation free energy of III-V semiconductors and their oxide bonding [12].

III-V semiconductor and oxide	Standard free energy of formation ΔG_f (kcal/mol)
GaAs	-16.01
InAs	-12.81
AlAs	-25.45
As ₂ O ₃	-138
Ga ₂ O ₃	-242.04
In ₂ O ₃	-198.55
Al ₂ O ₃	-378.08
As	3.18