Atomic layer deposition of HfO_2 on III-V semiconductors – an interfacial chemistry perspective

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ABSTRACT

The atomic layer deposition (ALD) of HfO_2 on various III-V semiconductor materials is discussed in detail, with particular emphasis on the interaction between the HfO_2 and the residual native oxide present at the interface. This interface is of critical importance in terms of device performance, impacting on the interfacial trap density which can lead to Fermi level pinning. Changes in the interfacial chemistry between ALD HfO_2 and GaAs, InGaAs and InP are discussed in terms of changes to the composition of the native oxide upon interaction with the ALD precursors, as well as the potential for migration of substrate materials into the high-k oxide layer.

Keywords: HfO_2, III-V semiconductor, ALD, InGaAs, InP

1 INTRODUCTION

With the continued scaling of silicon based semiconductor devices, the incorporation of a high-k dielectric layer to mitigate the potential for electron tunneling from the gate electrode through the gate dielectric to the channel has become a necessary step to improve device performance.[1] As a result, the introduction of alternative semiconductor materials for the channel region in many field effect devices, such as graphene and III-V semiconductor materials (InGaAs, InP, GaSb etc.) is under examination. [2,3]

To some degree, the integration issues involved with incorporating a high-k dielectric on Si is similar to the issues that arise for other semiconductor materials (deposition methods, ensuring sufficient band offsets etc). However there are some significant issues that need to be investigated for each individual material system to fully understand the impact of introducing an oxide layer on the semiconductor surface. For silicon, high-k oxidation is relatively easily controlled, with the initial interface typically consisting of a silicate which is able to retain a low interfacial trap density (D_{it}) and elevated dielectric constant over SiO_2 alone.[4] However, in the case of III-V semiconductors, this oxide interface is much more complex, with the native oxides on these surfaces typically consisting of numerous individual chemical states which are extremely sensitive to modest changes in processing conditions.[5] These can contribute significantly to the D_{it}, many having energy levels which place them in the semiconductor band-gap, or contribute to the formation of surface states which do.[6,7] This can potentially lead to Fermi level pinning and greatly impact on device performance. Understanding the chemical composition of the native oxides as well as the interactions they undergo upon deposition of a high-k oxide and the native oxides is therefore of significant importance. While thermodynamics has a large part to play, surface kinetics and the valency of the different oxide states also plays a big role, and considering the complex makeup of the native oxides which are hard to model theoretically, it is extremely hard to predict the reactions that will take place.[8] For this reason experiments designed to identify what is happening during the initial stages of oxide growth are of significant importance.[9]

In this report we discuss the current state of understanding regarding the ALD depositon of HfO_2 on GaAs, InGaAs and InP, in terms of changes to the native oxides upon interaction with the ALD precursors, chemical treatments that can help improve this interface prior to ALD, and further comment on the thermal stability of the substrate constituents though the deposited oxide layer during deposition. HfO_2, having a dielectic constant of ~25 and a band gap of approximately 6 eV, sufficiently wide enough to ensure good band alignment with most III-V semiconductor materials, has been extensively investigated, and is currently incorporated in the dielectric layer of the latest generations of high quality Si based devices.

2 INTERFACIAL REACTION STUDIES

2.1 Atomic Layer Deposition of HfO_2

Recent studies have investigated the initial growth conditions of ALD HfO_2 on various III-V semiconductor substrates.[10] It has been shown that the Hf precursors are able to interact with the native oxides present on the surface, and particularly in the case of III-As based

materials, a "clean up" or interfacial "self cleaning" process is observed to take place.[11] The native oxides are observed to decompose, with oxygen transferring form the native oxide, resulting in the formation of HfO_2. The interaction with the precursor is seen to progress through a ligand exchange mechanism,[12] with different oxide states seen to decrease preferentially over others during the "cleanup" process depending on the valency of the individual oxide states. In the case of case of As-O states on GaAs and InGaAs, a decrease in As_2O_5 like states is seen to take preferentially over As_2O_3 with HfO_2 deposition, whereas upon deposition of Al_2O_3, the As_2O_3 state is observed to preferentially interact with the trimethyl-aluminum precursor.

However, the "clean up" effect is seen to be substrate dependent. On InP, upon deposition of HfO_2, while there is some decrease in the In-O states present on the surface, the phosphorous oxide concentration is not observed to change, however the interaction with the ALD precursors does instigate a change in the composition of the P-O states, likely changing from initial $InPO_4$ and P-OH like states into the more phosphorous rich $In(PO_3)_3$ like state. This has implications for device performance, as we have recently reported a correlation between an increase in these states and a concomitant increase in D_{it}.[13]

One issue that is not readily reported is what happens to the substrate component of the decomposed native oxide species during the deposition process. Where this takes place at the surface during the initial stages of the deposition process, it is fair to assume that the majority are liberated from the surface through bonding to the volatile reacted ALD species and purged from the reactor. However, where this takes place under a fully formed oxide layer, whether through competing chemical interactions or thermal decomposition of the oxides during deposition, the movement and location of these species is not so clear. In this study we look at the mass transport of substrate materials in HfO_2 during the ALD process on InGaAs and InP.[14]

2.2 Pre-ALD surface treatments

Methods to improve the III-V semiconductor/ HfO_2 interface prior to HfO_2 deposition are also widely investigated, with various *ex-situ* and *in-situ* methods used to reduce the concentration of native oxides present on the surface, and to control the level of interface states present. These range from wet chemical acid and base treatments, such as etching in HF, NH_4OH, HCl, piranha based solutions,[11,15,16] as well as S-based passivation processes, for example, $(NH_4)_2S$),[17] to in-situ surface pre-treatments, for example TMA dosing,[18] UHV annealing and metallic capping layer removal, and atomic hydrogen treatment, which uses cracked molecular H that reacts with the C and O on the surface creating volatile species, with the aim of leaving a contamination free surface.[19] However, significant optimization of these processes is still needed, with no clear process currently reported which provides a low enough interface state density for good device performance. Of these, $(NH_4)_2S$ treatment may be one of the most promising candidates, as it is shown to significantly decrease the concentration of native oxides present on a range of different III-V materials, and reduce the re-oxidation rate during sample atmospheric exposure, without roughening of the surface. This may need to be combined with other processes to further enhance the interface characteristics, possibly using atomic hydrogen to remove adventitious carbon, and subsequent TMA and N_2 plasma exposure [20] to further passivate defects and reduce $D_{it.}$

3 EXPERIMENTAL DETAILS

In these studies HfO_2 was deposited by ALD on InGaAs and InP substrates. In the case of InGaAs, $In_{0.53}Ga_{0.47}As$ layers where grown on 50 mm sulfur-doped InP(100) substrates (IQE doping ~ 3 to $8x10^{18}cm^{-3}$) .The buffer layer for growth of $In_{0.53}Ga_{0.47}As$ consisted of a 100 μm thick sulfur-doped InP (doping~$2x10^{18}cm^{-3}$). The top epitaxial layer of sulfur-doped $In_{0.53}Ga_{0.47}As$ (doping ~ 4 $x10^{17}cm^{-3}$) was 2000 µm thick. InP buffer and $In_{0.53}Ga_{0.47}As$ top epitaxial layers were grown using metal-organic vapor phase epitaxy.

HfO_2 (4 nm) was grown *ex-situ* on 3 samples cleaved from a single epi-ready 2-inch $In_{0.53}Ga_{0.47}As$ wafer using tetrakis ethylmethylamino hafnium (TEMAH) and water pulsed into an argon carrier flow at an operating pressure of approximately 0.1 torr (base pressure < $1x10^{-5}$ torr). One sample underwent no post depostion annealing, while the other two were annealed in either forming gas or N_2 at 350 °C for 30 mins at atmospheric pressures. Samples were stored under N_2 in a glove box prior to transfer to seperate ultra high vacuum systems for LEIS and XPS measurements.

For InP studies, 2 samples cleaved from a 50 mm S-doped InP(100) single crystal wafer were used (IQE doping ~ 1 x $10^{18}cm^{-3}$). One sample was degreased using a standard degrease process (1 min each in acetone, methanol and isopopanol) while the other sample first underwent the same degreasing process and was then dipped in $(NH_4)_2S$ (10% for 20 minutes at room temperature) and subsequently rinsed in DI water for 10 to remove residual $(NH_4)_2S$. The samples were then immediately loaded to UHV (within 7 minutes) and XPS was carried out to determine the initial starting conditions. Samples were than annealed at 400 °C for 30 mins in UHV.

HfO_2 was deposited *in-situ* using tetrakis(dimethylamido)-hafnium (TDMA-Hf) and water in a Picosun© ALD reactor, with a pulse time of 0.2 s and high purity (99.999%) N_2 purge time of 20 s, usung high purity N_2 as the carrier gas. The base pressure in this ALD reactor was ~7 torr, with samples transferred from the XPS analysis chamber to the ALD reactor under UHV conditions though a sample transfer tube maintained at < 1 x 10^{-10} mbar to prevent furhter contamination of the samples due to

atmospheric exposure. Approximately 5.6 nm (70 cycles TDMA-Hf and water at ~0.08 nm/cycle) of HfO_2 was deposited on both samples and again transferred under UHV and scanned by XPS.

XPS was carried out in all cases in a multi chamber *in-situ* analysis and deposition system, described in detail elsewhere, using a monochromated Al kα x-ray source (hν = 1486.7 eV) with spectra aquired using a 7 channel hemispherical analyzer operating at a pass energy of 15 eV. XPS spectra were taken of the In 3*d*, Ga 2*p*, In 4*d*, Ga 3*d*, As 2*p*, As 3*d*, C 1*s*, O 1*s*, and Hf 4*f* core levels on the InGaAs samples, with P 2*p* and Hf 4*d* spectra also taken from the InP samples. Spectral peak deconvolution was preformed using AAnalyzer peak fitting software, which allows for independent control of the Gaussian and Lorentzian peak components, as well as dynamically fitting the peak background during the fitting process which provides for a much more accurate background subtraction. Low energy ion scattering spectroscopy was carried out uisng either 3 keV He^+ or 5 keV Ne^+ ions in a dedicated analysis chamber, with a base pressure of < 6 x 10^{-10} mbar. After advantitious carbon removal using a high dose of 5 keV Ne^+ ions, LEIS spectra from the HfO_2 surface were aquired using an ion dose of ~7 x10^{13} /cm^2.

4 RESULTS

The depositon of HfO_2 on InGaAs, results in the decrease of interfacial oxides at the HfO_2/InGaAs interface. However, looking at the ratio of the peak area of the As $2p_{3/2}$ and Hf 4*f* XPS core level spectra from the native oxide, FGA and N_2 annealed samples in Figure 1, the detection of an As signal is clear. However, the As 2*p* XPS core levels are extremely surface sensitive, with the effective atenuation length electrons coming from this core level being ~ 0.7 nm. This means that for a 4 nm HfO_2 film, the signal from the As 2*p* core level electrons originating in the substrate should be significantly below the XPS detection limits. This is the case for electrons from the Ga 2*p* core level, with no signal detected. This indicates that while there is no migration of Ga species in the HfO_2 layer, there is movement of As atoms.

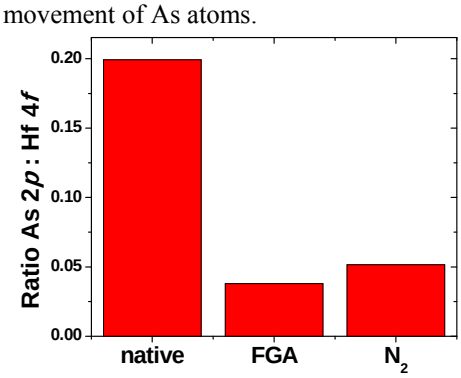

Figure 1. Ratio of As $2p_{3/2}$ to Hf 4*f* core level spectra from 4 nm HfO_2/InGaAs/InP samples for samples with no anneal, 300 °C anneal in forming gas, or 350 °C anneal in N_2 indicating As located at the surface and at elevated level on sample with no anneal.

The signal detected, particularly for the native and FGA samples is mostly in the form of As-O, is most likely due to re-oxidation As atoms, either in the HfO_2 film or when they are loacted at or close to the HfO_2 surface. This is reinforced by the fact that the As atoms are mostly in an unoxidised state in the N_2 annealed sample. In fact, the signal from the native sample is significantly greater than that from the other two samples, possibly suggesting that the anneals may play a role in removing some of these species from the HfO_2 film and top surface.

The LEIS spectra for the native oxide sample is shown in Figure 2, and is representative of the other two samples, with minor changes in the peak intensites. This indicates that along with As being presnt on the surface, there is also In detected. Detection of In in the XPS spectra was complicated by the presence of the Hf 4*p* core level and Ga *LMM* Auger components at similar binding energies. The presence of In and As oxides is well correlated with the thermal stability of the native oxides on InGaAs, with In oxides observed to decompose to preferentially form Ga-O states at temperatures as low as 150 °C, with the Ga-O states stable at >450 °C. The As oxides also begin to decompose at ~300 °C. This process could be catalyzed by interaction with the ALD precursors.

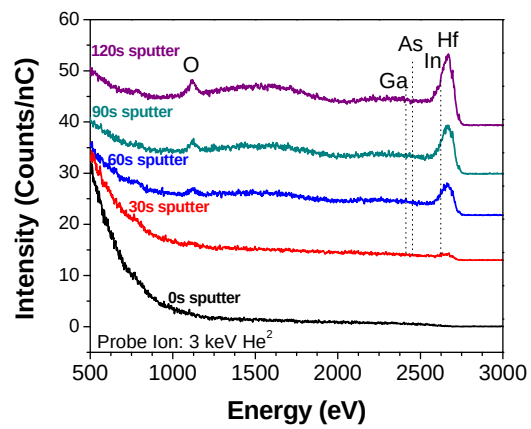

Figure 2. LEIS spectra of HfO_2 on InGaAs, from the native oxide sample, using a 3 keV He^+ ion source indicating the presence of In atoms on the surface of the HfO_2.

A similar result is also seen on InP, with an increase in the In-O signal detected after annealing in UHV at 400 °C as shown in Figure 3. Angular resolved XPS indicates that this is located primarily at, or close to the HfO_2 surface, indicating that it is not due to an increase in the interfacial oxide thickness. There is no change in the P 2*p* spectra within XPS detection limits. This could indicate that during HfO_2 deposition and anneal, there is generation of In-O at the interface, which is not thermally stable, causing it to migrate through the HfO_2 film, while the more stable P-O states remain at the interface. On the $(NH_4)_2S$ treated surface, the concentration of In detected is significantly lower than on the native oxide sample, suggesting the the S is playing a role in enhancing the stability of the InP surface.

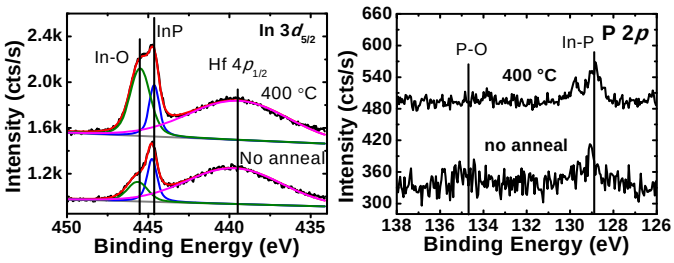

Figure 3. In 3*d* and P 2*p* core level spectra from HfO_2/InP samples before and after annealing indicating an incrase on In-O and virtually no change in the phosphorous.

5 CONCLUSIONS

HfO_2 deposited on III-V semiconductors is seen to interact with the native oxides present on the surface, decreasing the concentration of individual oxide species. However, during the deposition process and subsequent annealing, the presence of substrate materials close to the surface of the HfO_2 is detected. The presence of these species could have a detrimental impact on device perfromance, producing energetic defects throughout the oxide layer.

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