Interface characterization of metal-HfO$_2$-InAs gate stacks using hard x-ray photoemission spectroscopy


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MOS devices based on III-V semiconductors and thin high-k dielectric layers offer possibilities for improved transport properties. Here, we have studied the interface structure and chemical composition of realistic MOS gate stacks, consisting of a W or Pd metal film and a 6- or 12-nm-thick HfO$_2$ layer deposited on InAs, with Hard X-ray Photoemission Spectroscopy. In and As signals from InAs buried more than 18 nm below the surface are clearly detected. The HfO$_2$ layers are found to be homogeneous, and no influence of the top metal on the sharp InAs-HfO$_2$ interface is observed. These results bridge the gap between conventional photoemission spectroscopy studies on various metal-free model samples with very thin dielectric layers and realistic MOS gate stacks. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.

The continued development of Metal-Oxide-Semiconductor (MOS) devices requires more than scaling to increase the drive current and lower the power consumption. Promising strategies for improving the performance of MOS field-effect-transistors include the use of narrow band gap III-V semiconductors, gate oxides with a high permittivity such as Al$_2$O$_3$ or HfO$_2$, and advanced device geometries like wrap-gate nanowire transistors. Very thin homogeneous high-k oxide layers can routinely be formed by atomic layer deposition (ALD), where even a self-cleaning effect on the native oxide has been observed. Nevertheless, the stoichiometry of the interface between the III-V semiconductor and the high-k dielectric is still not fully controlled and plays a crucial role for the device performance.

X-ray photoelectron spectroscopy (XPS) has been proven a powerful technique to study the interface between high-k dielectric films and semiconductors like GaAs and InAs, the latter material being especially promising for electronic applications due to its large electron mobility and high electron injection velocity. Thereby XPS could accurately reveal the interface chemistry including quantitative suboxide evaluation, sources of interface defects, and stoichiometry variations within thin films. The high intensity and tunable photon energy of today’s synchrotron X-ray sources increases the resolution and further extends the limits of this method, enabling e.g. the investigation of nanowire interfaces. However, such investigations are limited to structures with very thin high-k layers and without any gate metal on top due to the small probing depth of conventional XPS. With typical photon energies of $h\nu < 2$ keV for both XPS lab sources and conventional synchrotron XPS endstations, the inelastic mean free path (IMFP) of the excited...
electrons and thus the probing depth of XPS is limited to about 2 nm. Electrical measurements like current-voltage (I-V) or capacitance-voltage (C-V) spectroscopy, on the other hand, can only be applied to full MOS structures with a top metal and a sufficiently thick high-k oxide layer that prevents leakage currents.\(^2,3\) Therefore no direct comparison between the device performance measured by I-V or C-V spectroscopy and the structural and chemical interface properties obtained by conventional XPS can be made, and all correlations are based on the non-trivial assumption that any influence of the oxide layer thickness and the impact of the top metal on the behavior of the MOS structure can be neglected.

Only the use of hard X-ray photoemission spectroscopy (HAXPES), where excitation energies even above 10 keV can be used, allows the chemically sensitive investigation of realistic MOS stacks in a non-destructive manner due to the larger kinetic energy and thus larger IMFP of the excited electrons. HAXPES studies on Si MOS structures have proven that the deposition of a high-k layer like HfO\(_2\) on Si leads to the formation of an interface layer, where different phases of Hf silicates and Hf-Si bonds have been observed,\(^19\) and the stoichiometry of the HfO\(_2\) layer changes over a thickness of several nm.\(^20\) Similar complex interface layers have also been found at Ge MOS structures.\(^21\) Furthermore, significant band bending effects of the top metal on the semiconductor-oxide interface may be expected.\(^22\) However, only little is known about the interface between the high-k oxide layers and the III-V semiconductors in full MOS stacks. Thus, there is an eminent need to investigate these interfaces, the homogeneity of thicker oxide layers, and the influence of the top metal. Thereby we evaluate how far the results from conventional XPS studies of thin oxide films on (In,Ga)As can be applied to realistic MOS structures.

In this work, we present HAXPES and X-Ray Reflectivity (XRR) data on InAs/HfO\(_2\)/metal-stacks with varying HfO\(_2\) thicknesses and with or without top metals. While most HAXPES experiments this far have been conducted using excitation energies between 6 and 8 keV, here we go to even higher energies of up to 20 keV. Thus we are able to investigate realistic MOS stacks with InAs material buried below oxide and metal layers of up to 18 nm in thickness. Through depth profiling we show that the HfO\(_2\) homogeneity does not change with varying thickness or top metal influence. A sharp InAs/HfO\(_2\) interface with no significant amount of As-oxides is observed.

Four different MOS structures consisting of n-type InAs (100) substrates, a 6- or 12-nm-thick HfO\(_2\) film, and an about 6-nm-thick Pd or W film were investigated. The epi-ready InAs substrates were etched with HF:H\(_2\)O (1:10) for 60 s, and rinsed in isopropanol for 15 s. Either 80 or 150 cycles of HfO\(_2\) were grown using tetrakis-dimethylamido-hafnium (Hf((CH\(_3\))\(_2\)N)\(_2\)) and water as precursors at a deposition temperature of 250°C in a Cambridge Nanotech Savannah-100 ALD chamber starting with an Al-pulse. Top metal layers were fabricated by W sputtering or Pd evaporation, resulting in an about 6 nm thick film. Two samples with 6- or 12-nm-thick HfO\(_2\) but no top metal layer served as reference samples. HAXPES measurements were performed at the SpLine Spanish CRG Beamline at the ESRF synchrotron facility in Grenoble, France. This beamline is specially designed for HAXPES and surface X-ray diffraction experiments at photon energies between 9 and 45 keV, featuring a high photon flux generated by bending magnet D25 of the ESRF, an ultrahigh vacuum chamber with Be windows transparent to X-rays, and a high voltage electron analyzer with a retarding lens system specially developed in cooperation with Focus GmbH to study electrons with kinetic energies of up to 15 keV.\(^23\) With this setup, HAXPES data from a Ge film buried under 10-nm-thick oxide and metal layers\(^20\) and even from a thin LaCaMnO\(_3\) layer buried under 53 nm of SrTiO\(_3\)\(^24\) could be obtained.

X-ray reflectivity (XRR) data, as shown in Fig. 1, were measured at the beamline and fitted using the ESRF-developed software tool \textit{Xop} in order to evaluate the MOS layer thicknesses and interface roughnesses.\(^20,25\) The obtained HfO\(_2\) layer thicknesses were 5.9 ± 0.2 and 11.9 ± 0.3 nm, and the W and Pd layer thicknesses were 5.9 ± 0.4 and 5.4 ± 0.1 nm, respectively. These values agree very well with the expected values. The roughness of the InAs/HfO\(_2\) and HfO\(_2\)/metal interfaces were 0.4 and 0.2 nm, respectively, indicating a sharp interface extending over only one to two monolayers.

In 2p\(_{1/2}\), As 2p\(_{3/2}\), Hf 2p\(_{1/2}\), Pd 2p\(_{3/2}\), W 2p\(_{3/2}\), and O 1s core level spectra were recorded. Theses levels were chosen since they provide the maximum photoionization cross section at the high excitation energies of this study,\(^26\) also taking into account that the electron analyser could handle a maximum electron kinetic energy of 15 keV. In order to enable a systematic comparison
FIG. 1. The samples investigated were InAs with 6 or 12 nm HfO$_2$ and with 6 nm W or 5 nm Pd on top, as well as reference samples without any top metal. Measured XRR data (dots) and fit (line) (a) for sample with 12 nm HfO$_2$ and 5 nm Pd and (b) for sample with 6 nm HfO$_2$ and 6 nm W.

FIG. 2. (a) Typical HAXPES data showing an In 2p$_{3/2}$ core-level spectrum. Fitted components are indicated. (b) The signal intensity of: As 2p$_{3/2}$ attenuated by 6 nm (blue star) and 12 nm (blue circle) of HfO$_2$, and In 2p$_{3/2}$ attenuated by 6 nm (red star) and 12 nm (red circle) of HfO$_2$, recorded at different excitation energies. (c) The IMFP as obtained from the measured signal intensities (As: blue, In: red), together with theoretical values calculated using the G1 formula (green) and the TPP-2M (black).

and analysis of the recorded HAXPES spectra, a thorough peak fit procedure was implemented. A typical recorded spectra is plotted with blue circles in Fig. 2(a), consisting of the core level peak (red), in this case for In 2p$_{3/2}$, and a secondary satellite peak (green) at higher binding energy. The satellite peak is attributed to energy losses of the excited electron due to plasmon excitations. For further analysis of the interesting core level signal (red), a fit of these two peaks and the background (black) is required. The peaks are defined as Voigt profiles, while the background is fitted with a Shirley function to account for the asymmetry of the peaks in the spectra that is highly pronounced at the high excitation energies used. Larger excitation energies will increase the ratio between the amount of electrons excited from deep within the sample versus the amount of electrons excited at the surface reaching the detector. This, in turn, will give rise to more inelastically scattered electrons detected which give the asymmetry of the peaks at the higher binding energy side of the peak.

The photoelectron signal from the In 2p$_{3/2}$ and the As 2p$_{3/2}$ core levels from both reference samples (6- and 12-nm-thick HfO$_2$), recorded at photon energies of 11, 12, and 14 keV, were normalized to the intensity of the photon beam. The intensity of the core level signals, determined as the area underneath the fitted normalized peaks, is shown in Fig. 2(b). The measured intensity, $I$, is given by:

$$I = I_0 e^{-d/\lambda},$$

where $I_0$ is the intensity of the excited electrons, $d$ the thickness of the HfO$_2$ layer, and $\lambda$ is the IMFP of the electrons traveling through the HfO$_2$. Here we make the assumption that the photoexcited electrons originate from the top most part of the III-V material and that the level of photomission excitation is the same for both reference samples (6 and 12 nm of HfO$_2$). In addition,
we assume sharp interfaces, as confirmed by the XRR data discussed above, and we take into account the detection angle (15° of normal), increasing the effective thickness of the HfO2 layer for the photoexcited electrons by a factor \[ \cos(15°)^{-1} \]. By comparing our two samples with different HfO2 layer thicknesses, we can write the expression:

\[
\lambda = \frac{6 \text{nm}}{\ln \left( \frac{I_{\text{HfO}_2}}{I_{\text{InAs}}} \cos(15°) \right)} ,
\]

where \( \lambda \) will be determined if the ratio between the signal intensities is known. Fig. 2(c) shows the experimental values for the IMFP for electrons in HfO2, as a function of kinetic energy, using this method. Blue circles are data obtained from As 2p3/2 core levels, red circles are In 2p3/2. The solid lines show theoretical values using the G1 (green)\(^\text{30}\) and the TPP-2M (black)\(^\text{31}\) formula, indicating that an extrapolation of the G1 formula agrees better with our measurements than the TPP-2M values. We fit our experimental data using the modified Bethe equation for the IMFP:\(^\text{31}\)

\[
\lambda = \frac{E}{E_p \left[ \beta \ln \left( \frac{E}{E_p} \right) - \left( \frac{E}{E_p} \right) + \left( \frac{E}{E_p} \right)^2 \right]} ,
\]

where \( \lambda \) is measured in Å, \( E \) is the electron energy measured in eV, \( E_p \) is the bulk plasmon energy (eV), and \( \beta, C, \) and \( D \) are parameters. For the fit of our data, the last two terms in the denominator are omitted due to the high energies used (\( C = D = 0 \)). With \( E_p = 16 \text{ eV}^{,32} \) the best fit with an rms value of 4.3 Å is obtained for \( \beta = 0.063 \left( \frac{0.042}{2} \right) \text{ eV}^{-1} \text{ Å}^{-1} \) and \( \gamma = 0.027 \left( \frac{0.061}{2} \right) \text{ eV}^{-1} \), values in parentheses are calculated using the TPP-2M formula.

Fig. 3(a) shows the In 2p3/2 signal and Fig. 3(c) the As 2p3/2 signal from a sample with 12 nm HfO2 and 6 nm W on top of the InAs. The spectra are recorded at 11, 12, 14, and 15.6 keV in descending order. Already at 11 keV excitation energy, when the electrons emitted from the In 2p3/2 core level have a kinetic energy of approximately 7.3 keV, the signal is clearly detectable even through 17 nm of combined oxide and metal, as demonstrated in Fig. 3(a). The signal to noise ratio is lower for As 2p3/2 compared to In 2p3/2 due to the lower photon-electron cross section for As 2p3/2 at these high excitation energies.\(^\text{33}\)

It should be noted that a rather strong peak broadening is observed in the spectra for higher excitation energies. The instrumental broadening is determined by the energy resolution of the analyzer and the monochromator, and with the instrumental settings used here (in order to obtain a high photon flux) it increases from 1.8 eV to 3.0 eV for excitation energies from 11 keV to 20 keV. The calculated natural linewidths of the core levels are 0.9 eV for As 2p3/2 and 2.7 eV for In 2p3/2. At 11 keV our experimental peak widths agree well with the expected values, but with increasing excitation energy the peak widths increase stronger than expected. In addition, the measured In 2p3/2 and As 2p3/2 peak positions are shifting over time by about 1 eV in a random fashion. Both observations might be explained by initial charging effects of the only weakly doped InAs substrates at higher photon energies.

Core level spectra obtained at different photon energies provide data with different information depths, due to the different IMFPs of the excited photoelectrons. Thus the In 2p3/2 and As 2p3/2 spectra in Fig. 3(a) and 3(c) represent depth profiles into the InAs. The measured binding energies of the In and As core levels have been calibrated using well-defined core levels of the W and Pd layers, which are unaffected by any band bending in the semiconductor. From the absence of systematic changes in peak shape or energy position in these depth profiles we can restrict possible band bending in the InAs to less than 0.5 eV. In addition, Fig. 3(b) shows the In 2p3/2 signal recorded at 14 keV for three different samples (all with 12 nm HfO2): no metal, 6 nm W, and 5 nm Pd on top, in descending order. No substantial influence of the top metals on the shape or energy position of the spectra can be seen, despite the large differences in work function \( \phi \) and electron affinity \( \chi \) for W (\( \phi = 4.55 \text{ eV}^{,34} \)), Pd (\( \phi = 5.12 \text{ eV}^{,35} \)) and HfO2 (\( \chi = 2.2 \text{ eV}^{,36} \)). This is an important observation regarding the validity of conventional XPS studies which are usually performed on samples with only a thin high-k layer, while realistic devices need a gate metal.

For the As 2p3/2 core level a large difference in binding energy between As-oxide peaks and As bound to In has been reported, amounting to 3 eV for As\(^{3+} \) (as in As\(_2\)O\(_3\)) and 4.5 eV for As\(^{5+} \) (as
FIG. 3. (a) The In 2p\textsubscript{3/2} signal at 11 to 15.6 keV excitation energy from sample with 12 nm HfO\textsubscript{2} and 6 nm W. (b) The In 2p\textsubscript{3/2} signal at 14 keV but from three different samples: reference sample with no metal on top, sample with W on top, and sample with Pd on top, in descending order. (c) The As 2p\textsubscript{3/2} signal, same as (a). (d) Hf 2p\textsubscript{3/2} signal, from sample with 12 nm HfO\textsubscript{2} and 6 nm W, with excitation energies ranging from 11 to 20 keV in descending order. (e) Hf 2p\textsubscript{3/2} signal from sample with 6 nm HfO\textsubscript{2} (squares) compared with Hf 2p\textsubscript{3/2} signal from sample with 12 nm HfO\textsubscript{2} (line), recorded with excitation energy of 15.6 keV. (f) Hf 2p\textsubscript{3/2} signal from reference sample with 12 nm HfO\textsubscript{2} (squares) compared with Hf 2p\textsubscript{3/2} signal from sample with 6 nm HfO\textsubscript{2} and 6 nm W (line) recorded with excitation energies of 20 keV. Spectra are shifted in height for better visibility.

in As\textsubscript{2}O\textsubscript{5}. However, our measured As 2p\textsubscript{3/2} peaks as those displayed in Fig. 3(c) are symmetrical and show no shoulders, with a full width at half maximum of only 2.1 eV (for 11 keV excitation energy). This indicates a strong reduction of the native As-oxides upon HfO\textsubscript{2} deposition, in good agreement with conventional XPS studies.

Depth profiles have also been obtained from the HfO\textsubscript{2} layers by studying the Hf 2p\textsubscript{3/2} core level with varying excitation energies, as shown in Fig. 3(d). All recorded spectra can well be fitted with a single symmetrical peak and without additional shoulders, indicating a homogeneous layer without changes in the hafnium oxidation state. The only change observed at the Hf 2p\textsubscript{3/2} spectra with increasing excitation energy is an increasing peak width, similar to the In 2p\textsubscript{3/2} and As 2p\textsubscript{3/2} core levels discussed above. In order to investigate the homogeneity of the HfO\textsubscript{2} layer more accurately, we compare the Hf 2p\textsubscript{3/2} signal from the sample with 12 nm HfO\textsubscript{2} and no top metal with that from the sample with 6 nm HfO\textsubscript{2} and no top metal, Fig. 3(e). These signals originate from the same depth of the HfO\textsubscript{2} layer and thus from different distances towards the interface with the InAs. In addition, we compare the peak shape of the Hf 2p\textsubscript{3/2} signal from the sample with 6 nm HfO\textsubscript{2} and 5 nm W with that from the sample with 12 nm HfO\textsubscript{2} and no top metal, Fig. 3(f). These signals in turn originate from different depths of the HfO\textsubscript{2} layer. In both cases, the compared spectra are almost identical.
should be noted that the observed broad Hf peak could also be explained by a convolution of several sub-components, representing a mixture of different Hf oxidation states, but also in this case the ratio of the different sub-components remains constant throughout the different samples and also within each HfO2 layer. With all our measurements put together, done at excitation energies ranging from 11 to 20 keV, we can conclude that the HfO2 is homogeneous in its composition throughout the entire thickness and that there is no effect on the HfO2 with respect to deposition of a top metal.

These results are in contrast to MOS structures with HfO2 on Si or Ge, where interface layers between the dielectric and the semiconductor play an important role. In Ge systems, due to Ge diffusion, an interface layer is shown due to the presence of Ge-Hf bonds in the HfO2.21,37 HAXPES studies on Si MOS structures have revealed several phases of different chemical bonding in the Si-HfO2 interface,19 leading to stoichiometry changes of the HfO2 over a thickness of several nm.20 Here, our HAXPES results do not show any evidence for the formation of an interface layer, instead the In and As signals in the semiconductor side as well as the Hf signal in the oxide side indicate homogeneous materials.

In conclusion, we have shown that realistic MOS gate stacks with a combined thickness of 18 nm of HfO2 and metal can well be studied using HAXPES. The clearly detectable In and As signals demonstrate a strong reduction of native As-oxides and give no indication of band bending within our energy resolution. The HfO2 layer is found to be homogenous, and no influence of the oxide thickness or the top metal on the stoichiometry of the HfO2 layer or the sharp InAs-HfO2 interface is observed. These results demonstrate that the semiconductor-oxide interface of model systems, consisting of (In,Ga)As substrates with only a thin HfO2 layer and no top metal, shows no significant differences to that of realistic III-V semiconductor based MOS structures. Therrwith it is actually eligible and highly useful to correlate conventional XPS studies on such model systems with the electrical performance of MOS transistors.

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