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Reduction of native oxides on InAs by atomic layer deposited AI_2O_3 and HfO_2

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Thin high- κ oxide films on InAs, formed by atomic layer deposition, are the key to achieve high-speed metal-oxide-semiconductor devices. We have studied the native oxide and the interface between InAs and 2 nm thick Al₂O₃ or HfO₂ layers using synchrotron x-ray photoemission spectroscopy. Both films lead to a strong oxide reduction, obtaining less than 10% of the native As-oxides and between 10% and 50% of the native In-oxides, depending on the deposition temperature. The ratio of native In- to As-oxides is determined to be 2:1. The exact composition and the influence of different oxidation states and suboxides is discussed in detail. © 2010 American Institute of Physics. [doi:10.1063/1.3495776]

The continuous demand for higher performance and lower power consumption in transistor technology has in recent years lead to a strongly increased interest in III-V metal-oxide-semiconductor (MOS) devices. Here the quality of the interfaces between III-V semiconductors and gate oxides with a large dielectric constant—so-called "high- κ " materials—is of crucial importance, since interfacial defects and native oxides on the semiconductor lead to frequency dispersion and hamper the electrical properties of gate transistors.^{1–4}

With the utilization of atomic layer deposition (ALD), the crystal and interface quality of a few nanometer thick high- κ layers such as Al₂O₃ or HfO₂ on GaAs and InGaAs have been significantly improved.⁵ Beside the total thickness of the remaining native oxide² also the exact stoichiometry and oxidation state of the Ga and As ions within this native oxide determine the device performance.⁶ Therefore, it is important to quantitatively investigate the chemical composition of the interface region between the III-V semiconductor and the high- κ oxide, which can best be done by core-level spectroscopy using x-ray photoemission (XPS).

Numerous XPS studies on high- κ gate dielectrics deposited by ALD on GaAs (Refs. 2 and 7) or InGaAs (Refs. 8 and 9) underline the promising potential of this system for application in high-speed MOS devices. However, although the electron mobility is larger in GaAs than in Si, it is further increased by about an order of magnitude in InAs.¹⁰ Additionally, InAs is an important binary reference material to the InGaAs material system. Studies by capacitance-voltage spectroscopy on high- κ thin films on bulk InAs (Refs. 11 and 12) as well as on InAs nanowires¹³ have recently been presented, but only a few XPS studies on high- κ thin films on InAs have been reported yet.¹⁴

In this work, we present XPS results on the interface between InAs and Al_2O_3 or HfO_2 layers deposited by ALD at different temperatures. A synchrotron source was used in

order to vary the energy of the photoemitted electrons and thus the probing depth. By thoroughly fitting the highresolution XPS core-level spectra of InAs-high- κ and InAs reference samples, we can reveal the composition of the native oxide and obtain quantitatively how the deposition of Al₂O₃ and HfO₂ layers reduces the different oxide components.

Nominally undoped InAs(100) substrates from Wafer Technology Ltd. were used for all samples. After removal of the epiready layer by heat treatment, the substrates were etched for 30 s in hydrofluoric acid, rinsed in isopropyl alcohol, and within a few minutes loaded into the ALD chamber, except for the reference samples. 24 cycles of either HfO₂ or Al₂O₃ were deposited in a Cambridge Nano-Tech Savannah 100 ALD reactor using tetrakis (dimethylamido)hafnium (Hf[(CH₃)₂N]₄) and trimethylaluminum (Al(CH₃)₃), resulting in about 2 nm thick films. Deposition was started with a single Hf pulse or a double Al pulse, respectively. Standard temperatures were 250 °C for HfO₂ and 350 °C for Al₂O₃. After ALD, the samples were kept in air for a few days.

XPS was performed at beamline I311 of the MAX II synchrotron ring.¹⁵ In 3d, In 4d, As 3d, O 1s, Hf 4f, and Al 2p core-level spectra were taken at photon energies varied between 70 and 1330 eV. All spectra were fitted selfconsistently with the FITXPS package assuming a Doniach-Sunjic line form, resulting for the As 3d (In 3d) core-level in a spin-orbit splitting of 0.67 ± 0.01 eV $(7.56 \pm 0.01 \text{ eV})$, a branching ratio of 1.52 ± 0.04 (1.50 ± 0.02) , a Lorentz width of 0.15 ± 0.03 eV $(0.31 \pm 0.05 \text{ eV})$, an asymmetry factor $\alpha = 0.030 \pm 0.004$ (0.003 ± 0.001), and a Gauss width of the InAs bulk peak between 0.4 and 0.5 eV (0.4 and 0.6 eV), in very good agreement with literature. $^{16-18}$ Strong background components are observed both in the As and In spectra of all high- κ samples due to inelastic electron scattering within the 2 nm thick oxide layer. Many samples were loaded in the XPS chamber simultaneously, so that the relative binding energies of their spectra can be compared with high accuracy and energy resolution.

Figure 1(a) compares As 3d spectra of a reference sample, an InAs/Al₂O₃ sample, and an InAs/HfO₂ sample,

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FIG. 1. (Color online) XPS As 3*d* spectra of a reference, an InAs/Al₂O₃, and an InAs/HfO₂ sample. (a) Sample comparison. The spectra are normalized and shifted for clarity. [(b)–(d)] Fitted data. In (d) an additional Hf 5*p* 1/2 peak needs to be considered. A constant part of the actually larger background in (d) is subtracted from the curves for clarity.

showing the influence of the high- κ film on the native oxide: The doublet at a binding energy around 41 eV comes from arsenic bound to indium, and the broad peak at about 44 eV is caused by arsenic bound to oxygen. Thus, a strong As-oxide signal is obtained for the reference sample, while both high- κ samples contain only very little As-oxide. The amount of native oxide on the reference samples was observed to be almost stable after less than ten minutes. Therefore, also the InAs/HfO₂ and InAs/Al₂O₃ samples must have had a similar native oxide layer prior to ALD, which was then reduced by the high- κ material.

To study the oxide reduction in more detail, fitted spectra are shown in Figs. 1(b)–1(d) for the different samples. It can be seen that two doublet components are necessary to fit the native oxide peak, a larger one at 3.2 eV and a smaller one at 4.3 eV above the bulk InAs binding energy, with Gauss widths of 0.9 eV and 1.2 eV, respectively. They can be identified as arsenic in a +3 oxidation state (like As₂O₃) and in a +5 oxidation state (like As₂O₅).^{18,19} A substantial reduction of both oxide peaks by the high- κ material is obtained from the spectra: The oxide peak of the InAs/Al₂O₃ as well as of the InAs/HfO₂ samples typically reaches less then 10% of the corresponding oxide peak size at the reference samples, corresponding to less than 0.1 nm layer thickness, for all photon energies. The Al₂O₃ films seem, however, to be more efficient than the HfO₂ films to also reduce the As⁵⁺ oxide component.

Concentrating now on the In peaks, a very thorough spectra fitting is required to analyze the oxide composition, since the bulk In-As and the In-oxide peaks overlap. Figures 2(a)-2(d) show a comparison as well as individual In 3d spectra of a reference sample, an InAs/Al₂O₃ sample, and an InAs/HfO₂ sample. Only one oxide peak is fitted, with a Gauss width of about 1.2 eV, which is dominating the In-As bulk peak at the reference samples, but gets significantly reduced by the high- κ layers: At the InAs/Al₂O₃ samples, the oxide peak typically has about 40%–50% the magnitude of the corresponding peak of a reference sample, while in the InAs/HfO₂ samples the oxide is slightly less reduced, show

FIG. 2. (Color online) [(a)-(d)] XPS In 3*d* spectra of a reference, an InAs/Al₂O₃, and an InAs/HfO₂ sample. (a) Sample comparison. The spectra are normalized and shifted for clarity. [(b)-(d)] Fitted data. (e) Fitted XPS In 4*d* spectrum of a reference sample. Two different In-oxide peaks can be distinguished.

ing 50%-70% of the corresponding reference oxide size, as summarized in Fig. 3(a).

For both high- κ materials, the separation in binding energy between the fitted In-As bulk and In-oxide peaks is about 50 meV larger than for the reference sample. An Inoxide consisting of two suboxides with different In oxidation states, where the high- κ films reduce that with the lower oxidation state stronger, would lead to the observed shift of the oxide peak energy. This might be important for applications, since in the well-known GaAs system the Ga³⁺ suboxide Ga₂O₃ is responsible for a strong decrease of device performance, while the Ga¹⁺ suboxide Ga₂O has less influence.⁶ The oxides of the InAs material system are more complex but by fitting an In 4d spectrum of a reference sample, as shown in Fig. 2(e), indeed two different In-oxide components get apparent. However, the fitting uncertainty is too large here to allow quantitative measurements of the oxide reduction.

reduced by the high- κ layers: At the InAs/Al₂O₃ samples, the oxide peak typically has about 40%–50% the magnitude of the corresponding peak of a reference sample, while in the InAs/HfO₂ samples, the oxide is slightly less reduced, show₅ subjects in Figs. 1 and 2. In (b) an additional shoulder needs to be considered to P

The stoichiometry of the native oxide is obtained from the relative heights of the oxide peaks in In 3d and As 3dreference spectra acquired at the same kinetic energy of the photoelectrons, amounting to $62\pm5\%$ In-oxide [see Fig. 3(a)]. By simulating the relative oxide and bulk peak sizes for each spectrum, the thickness of the native oxide film is obtained, which varies between 1.1 and 1.4 nm in the different reference samples. The As-oxide consists to about 80% of arsenic with the oxidation state +3, as in As₂O₃, and to about 20% of As⁵⁺, which can be assumed to As_2O_5 or the mixed oxide $InAsO_4$.¹⁸⁻²⁰ InAsO₄ as well as the stable Inoxide is In_2O_3 consist of In^{3+} . Since another In oxidation state is additionally observed, also In_2O (with In^{1+})¹⁴ or InO (with In^{2+}) could be present in the native oxide. Instead, also the existence of a single phase metastable nonstoichiometric oxide with microscopic units of different As and In oxidation states could well explain the observed data.¹⁸ Calculations of the Gibbs energy of formation have shown that InAsO₄ and In_2O_3 are energetically much more favorable than As_2O_3 or As_2O_5 ,²⁰ explaining the excess of In-oxide.

At the InAs/high- κ interface, the stoichiometry of the oxide has changed to about 90% In-oxide, as shown in Fig. 3(a). It has been reported that already the first cycle of Al₂O₃ deposition reduces most of the native oxide on GaAs,^{7,9} while on InAs an In-oxide peak related to In¹⁺ remains.¹⁴ However, when we repeated our XPS measurements on exactly the same InAs/HfO₂ and InAs/Al₂O₃ samples after several months, a much larger amount of both As- and In-oxides was observed, showing a reoxidation through the only 2 nm thick high- κ films under ambient conditions. Thus, already the originally measured interfacial oxide might be partly due to reoxidation after the sample preparation.

For high- κ layers deposited at standard temperatures of 250 °C for HfO₂ and 350 °C for Al₂O₃, no signs of aluminum or hafnium binding to indium or arsenic are observed in the corresponding spectra. Varying the HfO₂ deposition temperature to either 150 or 350 °C slightly decreases the oxide reduction but does not qualitatively alter the resulting spectra. The temperature of the Al_2O_3 deposition, however, is found to be of strong importance. Figures 3(b) and 3(c) show As 3d and In 3d spectra of an Al_2O_3 film deposited on InAs at 200 °C. In the As 3d spectrum, a shoulder at the high binding energy side of the InAs bulk peak is obvious, which can be fitted as an additional doublet with a 0.4 eV larger binding energy, indicating arsenic bonded to aluminum.²¹ In the In 3d spectrum, the In-oxide peak is significantly smaller than at the standard InAs/Al₂O₃ samples, reaching only 10% of the reference oxide peak size [Fig. 3(a)]. A possible explanation for both results could be the formation of a thin interfacial AlAs layer during ALD at this reduced temperature, which then protects (at least partly) the underlying InAs from being reoxidized later on.

In conclusion, we have studied the thickness and composition of the native oxide film on InAs. Strong oxide reduction is obtained by thin ALD films of Al_2O_3 or HfO₂, especially for As-oxides. These results underline the highly promising perspective for InAs MOS devices and contribute to an improved understanding of the complex processes taking place at the semiconductor high- κ interface.

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