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Citation: Applied Physics Letters 103, 142903 (2013); doi: 10.1063/1.4823584
View online: http://dx.doi.org/10.1063/1.4823584
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Demonstrating 1 nm-oxide-equivalent-thickness HfO$_2$/InSb structure with unpinning Fermi level and low gate leakage current density

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(Received 17 August 2013; accepted 14 September 2013; published online 30 September 2013)

In this work, the band alignment, interface, and electrical characteristics of HfO$_2$/InSb metal-oxide-semiconductor structure have been investigated. By using x-ray photoelectron spectroscopy analysis, the conduction band offset of 1.78 ± 0.1 eV and valence band offset of 3.35 ± 0.1 eV have been extracted. The transmission electron microscopy analysis has shown that HfO$_2$ layer would be a good diffusion barrier for InSb. As a result, 1 nm equivalent-oxide-thickness in the 4 nm HfO$_2$/InSb structure has been demonstrated with unpinning Fermi level and low leakage current of 10$^{-4}$ A/cm$^2$. The $D_a$ value of smaller than 10$^{12}$ eV$^{-1}$cm$^{-2}$ has been obtained using conduction method.

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InSb has been raised an attention for ultra-low power, high-speed field effect transistor (FET) application due to its high electron and hole mobility as compared to Si and other III-V compounds. Due to its narrow bandgap, InSb has been preferred to apply to quantum-well (QW), nanowire (NW), or tunnel (T) FET architectures. The high performance InSb-based QWFETs with very high-speed low supply voltage ($\leq 0.5$ V) have been demonstrated for both n- and p-channel devices. Both kinds of these devices have been showed much improvement in speed and power consumption as compared with start-of-the-art Si transistors. For those applications, the deposition of high k dielectric on InSb with good interface quality is very important for the effective performance of devices. Moreover, the scaling down of high k dielectric into sub-nanometer scale is of critical importance since devices have been getting smaller. In previous works, we have demonstrated that the electrical properties of Al$_2$O$_3$/InSb metal-oxide-semiconductor capacitors (MOSCAPs) are essential to the thermal (such as deposition and annealing) steps during the fabrication of devices. The low thermal budget of InSb would lead to the out-diffusion of Sb and In into Al$_2$O$_3$ layer under high temperature thermal step and thus, degrading the Al$_2$O$_3$/InSb interface as well as high k quality. In this work, we study the HfO$_2$/InSb structure, focusing on the band alignment, interface characteristics, and down scaling oxide thickness into sub-nm. It is found that HfO$_2$ can be a better diffusion barrier layer for InSb as compared to Al$_2$O$_3$. A 1 nm equivalent-oxide-thickness HfO$_2$/InSb MOSCAPs with good interface quality, unpinning Fermi level, and low leakage current is demonstrated.

Wafer used in this work are (100) n-type InSb substrate with doping concentration of 2.2 × 10$^{16}$ cm$^{-3}$ at room temperature. The process for the fabrication of MOSCAPs is similar to previous studies but HfO$_2$ gate oxide was used instead of Al$_2$O$_3$. After degreasing in acetone and isopropanol, sample was dipped in HCl 4% solution for removing native oxides, following by rinsing in deionized water and blown dry by N$_2$ gas. Samples were then loaded into the atomic-layer-deposition (ALD) chamber (Cambridge NanoTech Fiji 202 DSC) within 5 min. In ALD chamber, several pulses of trimethylaluminium (TMA)/Ar were performed before the deposition of 40 cycles (CYC) HfO$_2$ at 250 °C using tetrakis-ethylmethylamino-hafnium (TEMAHf) and water as precursors. TMA/Ar pulses were used because TMA has an effect not only in further removing III-V’s native oxides but also reducing the dangling bonds at III-V surface. The use of TMA pretreatment could help to reduce defects at InSb surface by satisfying electron counting rule as proposed by J. Robertson and L. Lin. Experimentally, the deposition of a very thin layer of Al$_2$O$_3$ (2 CYC) before depositing HfO$_2$ has shown significant improvement of high k/InGaAs interface. After high k deposition, Ni/Au gate metal was formed via photolithography/e-beam evaporation/lift-off process. Finally, the Au/Ge/Ni/Au metal was deposited for backside ohmic contact and followed by post metal deposition annealing (PMA) at 250 °C, in N$_2$, for 30 s.

The band alignment of HfO$_2$/InSb structure is firstly evaluated. The valence band offset $\Delta E_V$ of HfO$_2$/InSb structure is determined from XPS spectra, via the following equation:

$$
\Delta E_V = E_{HfO}^{InSb} - E_{InSb}^{HfO} + (E_{InSb}^{VBM} - E_{HfO}^{VBM}),
$$

where $E_{HfO}^{InSb}$ - $E_{InSb}^{HfO}$ is the energy difference between Hf 4f and Sb 4d core levels measured in 3 nm HfO$_2$/InSb interface; $E_{InSb}^{VBM}$ and $E_{HfO}^{VBM}$ are the differences...
between valence band maximum (VBM) energies and corresponding Sb 4d core level in InSb and Hf 4f core level in 8-nm-thick HfO2/InSb, respectively. Figure 1 shows the Sb 4d, Hf 4f, and VBM spectra of the samples for valence band offset measurement. The procedure for extracting core levels and VBMs was similar to what has been done for Al2O3/InSb structure.10 From Eq. (1) and the data showed in Fig. 1, the value of $\Delta E_V \sim 3.35 \pm 0.1$ eV was extracted. The band gap of HfO2 was deduced from the O 1s energy lose spectra to be 5.3 \pm 0.1 eV (data not shown). By combining these two data with the InSb band gap of 0.17 eV at room temperature, the conduction band offset $\Delta E_C$ of HfO2/InSb structure is deduced to be 1.78 \pm 0.1 eV.

Figure 2 shows the Sb 3d plus O 1s and In 3d5/2 spectra of InSb surface before and after HCl cleaning, and HfO2/InSb interface after deposition and after annealing at 250°C for 30 s, respectively. Because the O1s and Sb 3d5/2 spectra are overlapped, the change of Sb-O bonds would be verified by Sb 3d5/2 spectrum. As shown in the In 3d5/2 and Sb 3d5/2 spectra in the Figs. 2(a) and 2(b), the Sb-O and In-O bonds were reduced after HCl cleaning, especially for In-O bonds. Compared to the InAs case by using the same HCl clean,13 the reduction of In-O bonds is similar but the reduction As-O bonds is more significant than that of Sb-O bonds. The less significant reduction of Sb-O bonds might due to the rapid re-oxidation of Sb-O oxides during air exposure after HCl clean. After loading into ALD chamber and depositing high k, there is a reduction of Sb-O bonds as indicated in Fig. 1(c), Sb 3d5/2 spectrum. This reduction might come from two reasons (1) the self-cleaning effect by TMA pre-clean step9,16 and (2) the Sb-O oxides changed to In-O oxides via reaction: Sb2O3 + 2InSb $\rightarrow$ In2O3 + 4Sb (because the Gibbs free energy of In2O3 is lower than that of Sb2O3: $-198.6$ kcal/mol as compared to $-151.5$ kcal/mol).17 The reaction results in the increase of In-O bond as indicated in the Fig. 1(c), In 3d5/2 spectra. After annealing, almost Sb-O oxides changed to In-O oxides as indicated by the reduction of Sb-O signal to below the XPS detection level and a further increase of In-O signal (Fig. 1(d)).

The high-resolution transmission electron microscopy (HRTEM) image with the energy-dispersive X-ray spectroscopy (EDX) analysis is shown in Fig. 3. As shown in the figure, the total thickness of gate stack is $\sim 4$ nm, including 0.8 nm interfacial layer which is attributed to the out-diffusion of In, Sb into HfO2 during thermal processes. For the Al2O3/InSb structure with very similar fabrication

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**FIG. 1.** XPS spectra of (a) Sb 4d core level and valence band of InSb surface (after HCl cleaning), (b) Hf 4f and In 4d core levels at the 3 nm HfO2/InSb interface, and (c) Hf 4f and valence band of 8 nm HfO2 film.

**FIG. 2.** In 3d5/2 and Sb 3d plus O1s XPS spectra of (a) native InSb surface, (b) as HCl treated InSb surface, (c) as deposited HfO2/InSb interface, and (d) HfO2/InSb interface after annealing at 250°C, in N2, for 30 s.
process, a 1.5 nm-thick interfacial layer was observed. This implies that HfO₂ would be a good diffusion barrier for InSb. The EDX spectra clearly indicate that the Sb, In signals are under detection level of EDX measurement in the HfO₂ bulk layer. Ni gate metal also did not diffuse into HfO₂ during the PMA step as indicated by EDX spectra in the figure.

Next, the electrical properties of the MOSCAPs are investigated. The multi-frequency capacitance-voltage (C-V) curves at different temperatures (77 K, 150 K, and 300 K) of the sample are shown in Figs. 4(a)–4(c). At room temperature (300 K), the sample exhibits low frequency C-V behavior in whole measured frequencies (1 MHz–1 kHz). This is attributed to the very short minor carrier response time $\tau_R$ in InSb which was discussed in previous reports. Because of very short response time, minority carriers could response to high frequency ac signal and form an inversion layer when the gate voltage bias to negative side. From 300 K down to 77 K $\tau_R$ increases progressively, thus the C-V curves change gradually from the low frequency behavior at high temperature to the high frequency behavior at low temperature (77 K) and high frequency (100 kHz–1 MHz). This gradual changing indicates that Fermi level at HfO₂/InSb interface could move freely in the InSb bandgap. The unpinning Fermi level will be confirmed by using conduction map method as presented elsewhere. As shown in Fig. 4(a), the accumulation capacitance at room temperature can reach to 2900 pF/cm² at the gate voltage of 1.0 V. From that, the capacitance-equivalent-thickness (CET) is estimated directly from the relationship $\text{CET}(V) = \left(\varepsilon_{\text{SiO}_2} C(V)/\varepsilon_\infty\right) / C(V)$ ($\varepsilon_{\text{SiO}_2}$ is dielectric constant of SiO₂, $\varepsilon_\infty$ is the permittivity of free space, and C(V) is measured capacitance) to be about 1.19 nm. The equivalent-oxide-thickness (EOT) value extracted by taking into account of quantum-mechanical correction is generally lower that CET value. The difference between CET and EOT for is about several angstrom (0.43–0.47 nm for HfO₂/InGaAs MOS structure). From this point, the EOT value in this work is expected to be smaller than 1 nm. The current-voltage (I-V) characteristic of sample is shown in Fig. 4(d). The leakage current $10^{-4}$ A/cm² (at $V_{FB} + 0.5$ V) and breakdown field $E_{BD}$ of 5.9 MV/cm are adequate for the future logic devices application.

![FIG. 3. HRTEM image with the EDX analysis of the sample.](image)

![FIG. 4. Multi-frequency C-V characteristics of the sample at temperature of (a) 300 K, (b) 150 K, and (c) 77 K; (d) the leakage current-voltage characteristic of sample at 300 K.](image)
The conductance map method was applied to verify the interface density of states as well as the movement of Fermi level.\textsuperscript{19–21} The normalized parallel conductance is determined from the measured impedance by\textsuperscript{20,21}

\begin{equation}
G_p = \frac{1}{\omega qA} \times \frac{\omega C_{ox}^2 G_m}{G_m^2 + \omega^2 (C_{ox} - C_m)^2},
\end{equation}

where $A$ is the area of the MOSCAP, $\omega = 2\pi f$ ($f$ is frequency), $q$ is the elementary charge, $C_{ox}$ is the oxide capacitance, $C_m$ is the measured capacitance, and $G_m$ is the measured conductance. Because the conductance method is limited in the depletion region,\textsuperscript{19} only the measured data at 77 K and frequencies in range of 100 kHz to 1 MHz were selected for verifying. Figure 5(a) shows the normalized conductance contour as a function gate voltage and frequency (100 kHz–1 MHz) of the sample at 77 K. From the figure, the conductance peak maximum can shift along with gate bias and frequency (dashed line), indicating that Fermi level could move freely inside InSb bandgap. The interface density of states, $D_{it}$, was extracted from the maximum of normalized parallel conduction by

\begin{equation}
D_{it} = 2.5 \times \left( \frac{G_p}{\omega qA} \right)_{max}.
\end{equation}

The trap levels $E_T$ can be estimated from the trap response time $\tau_T = 1/f$ which is given by the Shockley–Read–Hall statistic\textsuperscript{21,22}

\begin{equation}
\tau_T = \frac{1}{f} = \frac{1}{\sigma v_{th} N} \times \exp(\Delta E/kT),
\end{equation}

\begin{equation}
\Rightarrow \Delta E = kT \ln \left( \frac{\sigma v_{th} N}{f} \right),
\end{equation}

where $\Delta E = E_C - E_T$ is the energy different between trap level and majority carrier band edge energy (conduction band in this case), $\sigma$ is the capture cross section of the trap ($\sigma = 10^{-16}$ cm$^2$ was taken in this work), $v_{th}$ is average thermal carrier velocity, $N$ is the effective density of state (DOS) in majority carrier band, $k$ is the Boltzmann constant, and $T$ is temperature. At temperature 77 K, the values of $v_{th} = 5 \times 10^7$ cm/s, $N = 5.4 \times 10^{15}$ cm$^{-3}$, and InSb bandgap of 0.23 eV were taken.\textsuperscript{1} For the frequency in range of 100 kHz to 1 MHz, the traps with energy level from 0.01 to 0.025 eV below the InSb conduction band edge $E_C$ (i.e., 0.22 to 0.205 eV above the InSb valence band edge $E_V$) would be extracted. The calculation also took into account the limitation of conductance method that the value of $D_{it}$ is reasonable only if $C_{ox} > qD_{it}$. The $D_{it}$ distribution as a function of trap energy levels of the sample is shown in Fig. 5(b). From the figure, the low $D_{it}$ of $6 \times 10^{11} - 1 \times 10^{12}$ eV$^{-1}$cm$^{-2}$ in the energy range of 0.22–0.205 eV above InSb valence band maximum has been obtained.

In conclusion, we have characterized the properties of the HfO$_2$/InSb MOS structure by using XPS, TEM, I-V, and C-V measurement. The band alignment of the HfO$_2$/InSb structure including conduction band offset of 1.78 ± 0.1 eV and valence band offset of 3.35 ± 0.1 eV has been deduced by XPS. The reduction of InSb native oxides via surface clean and thermal annealing steps has been verified. The TEM in conjunction with EDX analysis implied that HfO$_2$/InSb MOSCAPs have been demonstrated with low leakage current of $10^{-4}$ A/cm$^2$ at $V_{FB} + 0.5$ V. Unpinning Fermi level and the $D_{it}$ value of smaller than $10^{12}$ eV$^{-1}$cm$^{-2}$ has been demonstrated by C-V characteristics and conductance method. These good results would give a benefit for future realizing the InSb-based MOS devices application.

This work was supported by NCTU-UCB I-RiCE Program, Taiwan and Vietnam National Foundation for Science and Technology Development (Contract No. 103.02-2011.12).\textsuperscript{3}

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