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Energy band alignment of atomic layer deposited HfO₂ on epitaxial (110)Ge grown by molecular beam epitaxy

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The band alignment properties of atomic layer HfO₂ film deposited on epitaxial (110)Ge, grown by molecular beam epitaxy, was investigated using x-ray photoelectron spectroscopy. The cross-sectional transmission electron microscopy exhibited a sharp interface between the (110)Ge epilayer and the HfO₂ film. The measured valence band offset value of HfO₂ relative to (110)Ge was 2.28 ± 0.05 eV. The extracted conduction band offset value was 2.66 ± 0.1 eV using the bandgaps of HfO₂ of 5.61 eV and Ge bandgap of 0.67 eV. These band offset parameters and the interface chemical properties of HfO₂/(110)Ge system are of tremendous importance for the design of future high hole mobility and low-power Ge-based metal-oxide transistor devices.

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With the scaling of Si complementary metal-oxide semiconductor (CMOS) technology, each transistor has become smaller and faster leading to unprecedented increase in microprocessor performance. In future, transistor scaling will require the introduction of high mobility channel materials, including III-V and Ge, and device architectures. According to the International Technology Roadmap for Semiconductors, channel materials with superior transport properties, high-k gate dielectric, and multi-gate transistor configuration in a CMOS logic device under 10 nm regime are required to achieve further increase in transistor drive current and resultant ULSI performance improvement. In recent years, low bandgap high electron mobility III-V compounds coupled with high-k gate dielectrics have been demonstrated in n-channel device configuration operating at 0.5 V. However, the demonstration of a high hole mobility p-channel device configuration along with high-k dielectric is mandatory to realize energy-efficient CMOS logic. For this reason, the enhancement of carrier transport properties in the channel using high hole mobility channel materials, different surface orientations to improve the carrier mobility, and optimal channel direction have been proposed for further enhancement of CMOS devices. Very recently, it has been demonstrated that the carrier mobility of Ge can be enhanced by utilizing a Ge channel with different orientations; the carrier mobility was expected to be high in (111)Ge for electrons and in (110)Ge for holes. In fact, transistors fabricated on (110)Ge substrates exhibited higher hole mobilities of ~650 cm²/Vs along ⟨110⟩ direction. Dissanayake et al. have reported that the hole mobility of (110)Ge channel orientation along the ⟨110⟩ direction exhibited 2.3 times higher hole mobility compared with the ⟨100⟩Ge surface and thus have a potential advantage for p-channel field-effect device operation.

Significant research on the high-k gate dielectrics HfO₂, ZrO₂, Al₂O₃, Y₂O₃, Lu₂O₃, CeO₂, rare earth oxides, as well as germanium-oxynitride have been conducted on the (100)Ge metal-oxide semiconductor devices, hoping that the integration of high-k dielectrics with Ge will not only allow continued scaling of transistors but will also provide higher low-field intrinsic carrier mobility for improving device speed. Although excellent device performances were achieved using high-k gate dielectrics on (100)Ge and oxided/(100)Ge band alignment properties, little attention has been devoted towards the integration of high-k gate dielectrics on the (110)Ge and the associated energy band alignment at the interface. High-quality dielectric on (110)Ge interface is essential to eliminate the formation of high density intrinsic defects with energy levels in the semiconductor band gap due to poor quality native oxides, resulting in Fermi level pinning at the oxide-semiconductor interface. Furthermore, the selected high-k material should have valence and conduction band discontinuities larger than 1 eV relative to the semiconductor channel material to act as a barrier for both holes and electrons.

In this letter, we report on the band alignment properties between the atomic layer HfO₂ deposited on top of the epitaxial Ge grown on (110)GaAs substrate using solid source molecular beam epitaxy (MBE). The investigations were conducted by using x-ray photoelectron spectroscopy (XPS). The experimental results from this study are the first step towards achieving high-performance Ge channel material on (110)GaAs for p-channel field-effect transistor, which can be ultimately heterogeneously integrated to Si substrate through a III-V buffer layer for the realization of ultra-low power and high-speed CMOS logic.

The undoped epitaxial 60-80 nm thick Ge layers were in-situ growth process on (110) epi-ready GaAs substrates using separate solid source MBE growth chambers for Ge and III-V materials, connected via ultra-high vacuum transfer chamber. Substrate oxide desorption was done at ~580 °C under an arsenic overpressure of ~1×10⁻⁷ Torr in a III-V MBE chamber. An initial 0.2 μm undoped GaAs buffer layer was then deposited on (110)GaAs substrate to
generate a smooth surface at 550 °C under a stabilized As2 flux prior to transferring (110)GaAs wafer to the Ge MBE chamber for Ge epilayer growth. The growth temperature of Ge was ~400 °C. The detail of the growth procedure is reported elsewhere.\textsuperscript{31,32} The 1 nm and 5 nm HfO2 films were grown by atomic layer deposition (ALD) in a Cambridge NanoTech system on epitaxial (110)Ge using a Tetrakis(dimethylamino)hafnium compound as Hf precursor and H2O as the oxygen source. During the HfO2 growth, the surface temperature of (110)Ge film and Hf precursor temperature was kept constant at 250 °C and 75 °C, respectively. Epitaxial (110)Ge layers were cleaned using NH4OH:H2O2:H2O (2:1:1000 volume ratio) for 5 s prior to loading to ALD chamber for HfO2 deposition. The band alignment of HfO2/(110)Ge structures was investigated using a PHI Quantera SXM XPS system with a monochromated Al-Kα x-ray source.\textsuperscript{33} The Ge 3d and Hf 4f7/2 core level (CL) binding energy spectra as well as Ge and Hf valence band binding energy spectra were collected with a pass energy of 26 eV and an exit angle of 45°. The binding energy was corrected by adjusting the carbon (C) 1s CL peak position to 285.0 eV for each sample surface. Curve fitting was done by the CasaXPS 2.3.14 using a Lorentzian convolution with a Shirley-type background. The CL energy position was defined to be the center of the peak width at the half of the full width at half maximum. The bandgap of the HfO2 film,\textsuperscript{18,19} the core level, and valence electrons emitted from the film determined from the XPS measurement will allow to determine the valence band offset of HfO2 relative to the (110)Ge film by the method described in Ref. 32. The error bar we defined in this paper is due to the scatter of valence band spectra during the fitting of valence band maximum (VBM) position and considering the linearity and stability of the energy scale of the XPS binding energy spectrum.

Figures 1(a) and 1(b) show cross-sectional transmission electron microscopy (TEM) micrograph of HfO2/Ge/(110)GaAs structure and high-resolution TEM micrograph of HfO2/(110)GaAs interface, respectively. These TEM micrographs show a sharp interface between the Ge epilayer and the HfO2 film as well as Ge and (110)GaAs substrate. The HfO2 thickness measured by TEM is ~5 nm, consistent with the ALD deposited thickness. From Fig. 1(b), one can find that there is no interfacial layer formed during the deposition of HfO2 on (110)Ge layer which implies that the removal of unwanted interfacial oxide can be easily obtained on (110)Ge and thus have a potential advantage of high-k on Ge system.\textsuperscript{34}

As discussed earlier, the energy band alignment at the high-k/Ge interface is of great importance, since the sufficient barriers for electron and hole are needed to suppress the tunneling leakage current. Also, the reported hole mobility is higher on (110)Ge substrate, and the measured valence and conduction band offset values of HfO2 relative to (110)Ge will provide further insights into the predicted electrical transport mechanisms in the predefined Ge channel layer thickness grown on a large bandgap GaAs barrier layer. The valence band offset ΔEv at the HfO2/(110)Ge was determined using XPS system and angle integrated photoelectron energy distribution curves for the VBM. Using these methods, Ge 3d, Hf 4f7/2 core levels spectra were recorded. The peak separation of Ge 3d5/2 and 3d3/2 due to spin-orbit splitting is too small to be separated. The binding energy was corrected by adjusting the C 1s core-level peak position to 285.0 eV for each sample surface. XPS spectra were recorded from the following 3 samples: (i) (110)Ge epitaxial layer, (ii) 1 nm HfO2 on (110)Ge layer, and (iii) 5 nm thick HfO2 film on (110)Ge. Figures 2(a) and 2(b) show the Ge 3d core level \( E_{Ge}^{3d} \) spectrum of the (110)Ge film and VBM \( E_{VBM}^{Ge} \) (shown in inset) as well as Hf 4d7/2 core level \( E_{Hf}^{4d7/2} \) spectrum of 5 nm HfO2 film and VBM \( E_{VBM}^{Hf} \) (shown in inset), respectively.
Figure 3 shows the Ge 3d core level ($E_{\text{Ge}}^{\text{3d}}$) and Hf 4d_{7/2} core level ($E_{\text{Hf}}^{\text{4d_{7/2}}}$) spectrum of 1 nm HfO$_2$ on (110) Ge interface, respectively. The valence band offset, $\Delta E_V$ for a HfO$_2$/ (110)Ge interface, was determined from the following equation using core level spectra

\[
\Delta E_V = (E_{\text{Ge}}^{\text{3d}} - E_{\text{VBM}}^{\text{Ge}})^{\text{Ge}} - (E_{\text{Hf}}^{\text{4d_{7/2}}} - E_{\text{VBM}}^{\text{Hf}})^{\text{HfO}_2} - (E_{\text{Ge}}^{\text{3d}} - E_{\text{Hf}}^{\text{4d_{7/2}}})^{\text{HfO}_2/\text{Ge interface}},
\]

(1)

We have selected Hf 4f_{7/2} core level spectra rather than Hf 4f_{5/2} since the measured binding energy separation between the Hf 4f_{7/2} and Hf 4f_{5/2} peaks is fixed to 1.7 eV from each measurement. As a result, the band offset result would not change if we select Hf 4f_{5/2} as the core level binding energy peak. Finally, the conduction band offset, $\Delta E_C$ for a HfO$_2$(110)Ge interface is determined from the following equation:

\[
\Delta E_C = E_{\text{VBM}}^{\text{HfO}_2} - E_{\text{VBM}}^{\text{Ge}} - \Delta E_V,
\]

(2)

where $E_{\text{VBM}}^{\text{HfO}_2}$ and $E_{\text{VBM}}^{\text{Ge}}$ are the bandgaps of HfO$_2$ and Ge, respectively.

The position of the Ge 3d peak centroid from the XPS measurement was found to be 30.05 ± 0.005 eV as shown in Fig. 2(a). This value was obtained by measuring the center of the peak width at half of the peak height after Shirley background subtraction. The VBM for (110)Ge was determined as the intersection between the linear fits of the background and the linear portion of the VB leading edge, as shown in inset of Fig. 2(a). The energy difference between the Ge 3d centroid and the (110)Ge VBM was measured to be 29.36 ± 0.05 eV, providing excellent agreement with the results of HfO$_2$ on (100) Ge. Similarly, the energy difference between the Hf 4f_{7/2} centroid and the VBM was found to be 14.50 ± 0.05 eV for the 5 nm-thick HfO$_2$ film. For the 1 nm HfO$_2$ film on (110)Ge, the energy difference between the Ge 3d centroid and the Hf 4f_{7/2} core lines was determined to be 12.58 ± 0.05 eV. Using these measured data and Eq. (1), the measured value of $\Delta E_V$ for the HfO$_2$/(110)Ge interface is 2.28 ± 0.05 eV and this value is lower by ~0.6 eV than on (100)Ge substrate. To explain the observed differences in the $\Delta E_V$ values for the HfO$_2$ on (110)Ge and HfO$_2$ on (100)Ge, reflection high energy electron diffraction (RHEED) patterns were recorded from the epitaxial (110)Ge and (100)Ge layers and also from the starting GaAs substrates. The RHEED patterns from the surface of the Ge epitaxial layer were recorded after transferring the Ge epilayer from the Ge MBE chamber to the III-V MBE chamber. These RHEED patterns shed light on the reconstruction of epitaxial Ge layer grown on (100)GaAs and (110)GaAs substrates and thus the resulting band offset values of HfO$_2$ on (100)Ge and (100)Ge. A (100)Ge layer was deposited on a reconstructed (2$\times$4) GaAs surface with a surface layer being mainly arsenic exhibited (2$\times$2) surface reconstruction of Ge layer on (100)GaAs. On the other hand, the (110)GaAs surface exhibited a (1$\times$1) RHEED pattern, consistent with the other researchers and the deposited epitaxial Ge film on such surfaces.
surface oriented GaAs showed a streaky (3 x 4) RHEED pattern. As a result of different in surface reconstruction of Ge, the deposited band offset of HfO$_2$ on crystallographic oriented epitaxial Ge would exhibit different values of band offset. In fact, it has been reported that band offsets can depend on substrate orientation, overlayer crystallinity, surface reconstruction, deposition temperature, deposition rate, microscopic interface dipole, and interdiffusion or reactivity. Furthermore, the absence of interfacial layer at the microscopic interface dipole, and interdiffusion or reconstruction, deposition temperature, deposition rate, depend on substrate orientation, overlayer crystallinity, surface orientation, layer crystallinity, surface reconstruction, deposition temperature, deposition rate, microscopic interface dipole, and interdiffusion or reactivity.37

Figure 4 shows the band alignment diagram of the HfO$_2$/Ge heterojunction obtained from the present XPS results. The valence band and conduction band offsets are well above 1 eV, as needed for blocking electrons and holes for carrier transport in the fabricated Ge metal-oxide semiconductor field effect transistors. The transport properties will strongly depend on the interface states between the high-k and the (110)Ge layer. The band alignment of Ge on (110)GaAs substrate is included from Ref. 32. Thus, the measured band offset values on (110)Ge can provide a promising path for p-channel Ge field effect devices for low-power and high-speed computing platforms.

In summary, the experimental study of the band offset properties of HfO$_2$ on epitaxial (110)Ge grown by MBE was investigated using XPS. Cross-sectional TEM micrograph shows a sharp interface between the (110)Ga epilayer and the HfO$_2$ film. XPS results showed the valence band offset of 2.28 ± 0.05 eV at the HfO$_2$/(110)Ge heterointerface. The conduction band offset is calculated to be 2.66 ± 0.1 eV using the bandgap of HfO$_2$ of 6.71 eV and the well-known Ge bandgap of 0.67 eV. These band offset parameters and the interface chemical properties of the HfO$_2$/Ge system are vital for Ge-based p-channel metal-oxide transistor device design.

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FIG. 4. Energy-band diagram of the HfO$_2$/Ge heterojunction obtained from XPS measurements. The Ge/(110) GaAs band offset is included from Ref. 32.
37. L. J. Brillson, Surfaces and Interfaces of Electronic Materials (Wiley-VCH, Germany, 2010).