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3, 5001**Atomic layer deposited tantalum silicate on crystallographically-oriented epitaxial germanium: interface chemistry and band alignment**Michael B. Clavel, Shuvodip Bhattacharya and Mantu K. Hudait *

The interface chemistry and energy band alignment properties of atomic layer deposited (ALD) tantalum silicate (TaSiO_x) dielectrics on crystallographically-oriented, epitaxial (001)Ge, (110)Ge, and (111)Ge thin-films, grown on GaAs substrates by molecular beam epitaxy, were investigated. The ALD process, consisting of a 6:1 Ta:Si precursor super-cycle, was analyzed via sputter depth-dependent elemental analysis utilizing X-ray photoelectron spectroscopy (XPS). The XPS investigations revealed uniform Si incorporation throughout the TaSiO_x dielectric, and a measurable amount of cross-diffusion between Ge and Ta atomic species in the vicinity of the oxide/semiconductor heterointerface. The formation of a thin SiO_2 interfacial oxide, through the intentional pre-pulsing of the Si precursor prior to the Si:Ta super-cycle process, was observed via cross-sectional transmission electron microscopy analysis. Moreover, the bandgap of Ta-rich $\text{Ta}_{0.8}\text{Si}_{0.2}\text{O}_x$ dielectrics, analyzed using the photoelectron energy loss technique centered on the O 1s binding energy spectra, was determined to be in the range of 4.62 eV–4.66 eV (± 0.06 eV). Similarly, the XPS-derived valence band and conduction band offsets (ΔE_V and ΔE_C , respectively) were found to be $\Delta E_V > 3.0 \pm 0.1$ eV and $\Delta E_C > 0.6 \pm 0.1$ eV for the (001)Ge, (110)Ge, and (111)Ge orientations, promoting the increased carrier confinement necessary for reducing operational and off-state leakage current in metal–oxide–semiconductor devices. Thus, the empirical TaSiO_x/Ge interfacial energy band offsets, coupled with the uniform dielectric deposition observed herein, provides key guidance for the integration of TaSiO_x dielectrics with Ge-based field-effect transistors targeting ultra-low power logic applications.

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rsc.li/materials-advances**Introduction**

Despite continued innovations prolonging the longevity of the Si microelectronics industry, forward-looking research has regularly examined high carrier mobility, lower bandgap (E_g) materials as alternative channel materials in future complementary metal–oxide–semiconductor (CMOS) devices and integrated circuits (ICs). Germanium (Ge), in particular, is an attractive candidate due to its high electron and hole mobilities ($2\times$ and $4\times$ those of Si, respectively), and its tunable bandgap (either by alloying, strain incorporation, or both). Recently, high-performance CMOS inverters were demonstrated utilizing Ge p-channel (PMOS) and Si n-channel (NMOS) fin field-effect transistors (FinFETs), wherein the Ge layer/channel material was transferred onto a 300 mm Si wafer.¹ Although record-setting Ge PMOS performance was achieved in tandem with the lowest equivalent oxide thickness (EOT) to date, 5.7 Å, little was

revealed regarding the high- κ gate dielectric utilized. Moreover, the successful integration of Ge PMOS with $\text{In}_x\text{Ga}_{1-x}\text{As}$ NMOS (due to its high electron mobility), as opposed to Si NMOS, would revolutionize the ultra-low voltage landscape within the microelectronics industry. In such a configuration, several critical components are important to understand, including: (i) identification of a high- κ dielectric suitable for integration on crystallographically-oriented Ge, thus mimicking the surface orientation present in FinFET devices; (ii) the potential for atomic interdiffusion at the high- κ/Ge heterointerface (e.g., out-diffusion of Ge into HfO_2) or the underlying Ge/substrate interface (e.g., Ge-on-insulator, Ge/III–V, or Ge/Si); (iii) the energy band alignment between the high- κ dielectric and Ge (i.e., the valence and conduction band offsets, ΔE_V and ΔE_C , respectively), needed for understanding of channel carrier confinement; and (iv) thermal stability of the oxide/Ge interface, which would dictate process thermal budgets during dielectric deposition, annealing, and subsequent contact metalization stages. These coupled effects must be investigated in order to fully-utilize Ge-based technologies going forward.^{2,3} Whereas much recent work^{4–30} has focused on the $\text{HfO}_2/\text{Al}_2\text{O}_3$

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composite/bi-layer high- κ dielectric combined with an interfacial passivation layer (IPL), typically based on GeO_2 , it remains difficult to achieve sub-nm EOT. Thus, new passivation schemes have been proposed to realize highly uniform, compositionally abrupt, temperature-stable, and highly-scaled high- κ dielectric/Ge MOS interfaces.¹ In so doing, device designers have sought to mitigate direct-tunneling gate leakage current, which is exponential in nature, while maintaining superior gate-channel electrostatic coupling.³¹ Moreover, the process compatibility of future low-power technologies^{7–13,16–18,32,33} with existing Si CMOS infrastructure remains a key industry objective.

In order to address the above challenges, extensive dielectric research has been performed over the last two decades, with little success in finding simple (non-composite, or non-binary) dielectric systems that mimic the electrical and thermodynamic stability of the SiO_2/Si interface.^{4–38} One promising dielectric, tantalum oxide (Ta_2O_5), and its silicate (TaSiO_x or $(\text{Ta}_2\text{O}_5)_{1-x}(\text{SiO}_2)_x$), has recently found renewed interest as a potential high- κ dielectric for the Ge^{39–49} and III–V^{50–53} material systems. TaSiO_x was shown to achieve excellent device performance when integrated within a composite $\text{TaSiO}_x/\text{InP}$ gate stack (on $\text{In}_x\text{Ga}_{1-x}\text{As}$ -channel FETs), exhibiting low interfacial defect density (D_{it}), low gate leakage current density (J_{g}), and high drive current (I_{ON}).⁵¹ Thus, this study utilizes tantalum(v) ethoxide ($\text{Ta}_2(\text{OC}_2\text{H}_5)_{10}$) and tris(*tert*-butoxy)silanol ($\text{Si}(\text{OH})(\text{OC}(\text{CH}_3)_3)_3$) precursors (for Ta and Si, respectively) to investigate the atomic layer deposition process of $(\text{Ta}_2\text{O}_5)_{1-x}(\text{SiO}_2)_x$ onto crystallographically-oriented, epitaxial (001)Ge, (110)Ge, and (111)Ge. These precursors have been previously investigated for the deposition of metal silicates/oxides for high- κ gate dielectrics^{45,46} and SiO_2 -based IPLs between HfSiO_x dielectrics and their underlying Si substrates.⁴⁶ Alkylamide precursors can be operated at relatively low temperatures during dielectric ALD, and are an alternative to common amide precursors, such as tetrakis methyl-ethyl amino hafnium (TEMAH) or trimethyl aluminum (TMA) in the cases of HfO_2 and Al_2O_3 , respectively, which have been used in the past to deposit dielectrics exhibiting excellent performance. However, utilization of the common amide precursors has often been found to result in deleterious carbon incorporation into the as-deposited dielectric, which can adversely affect the electrical performance and reliability of the dielectric. *In this work*, crystallographically-oriented Ge thin-films were grown on GaAs substrates by an in-house, solid-source molecular beam epitaxy (MBE) deposition system.^{54–58} Cross-sectional transmission electron microscopy (X-TEM) analysis was used to determine the thickness of the as-deposited dielectric. X-Ray photoelectron spectroscopy (XPS) analysis was performed in order to study the valence and conduction band discontinuities, ΔE_{v} and ΔE_{c} , respectively at the $(\text{Ta}_2\text{O}_5)_{1-x}(\text{SiO}_2)_x/\text{Ge}$ heterointerface, as well as the chemical bonding environment at the interface. The development of a Ge-based FinFET device architecture, as exemplified in Fig. 1, requires specific understanding of the high- κ gate dielectric/semiconductor interface, including both the chemical and electrical characteristics of the combined material system. As such, the goal of this work is to demonstrate the feasibility of integrating

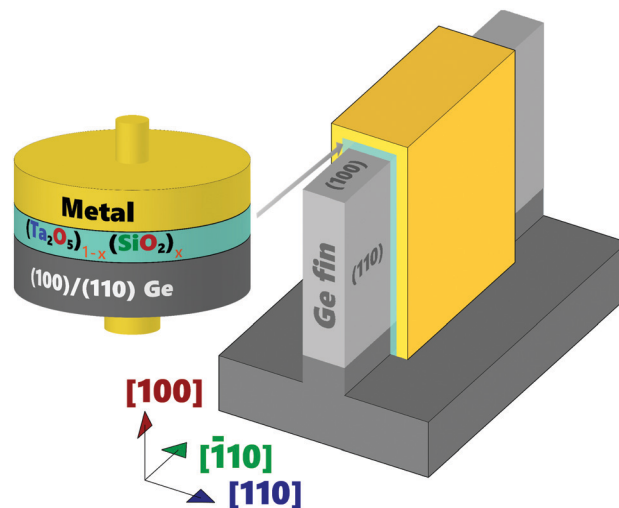


Fig. 1 Schematic representation of a Ge FinFET utilizing (001)Ge and (110)Ge surface orientations.

tantalum silicates (TaSiO_x) onto Ge by (empirically) elucidating the chemical nature/bonding environment of the TaSiO_x/Ge interface, as well as its electronic and physical structure.

Experimental

Crystallographically-oriented, epitaxial (001)Ge, (110)Ge, and (111)Ge thin-films were grown on epi-ready AXT Inc.-manufactured (001)GaAs, (110)GaAs, and (111)A GaAs substrates using a vacuum-interconnected, solid-source MBE system with isolated III–V and Ge growth reactors. GaAs native oxide desorption was performed using an arsenic (As) overpressure of $\sim 10^5$ Torr (inside the III–V growth chamber) utilizing a temperature range of 550 °C to 680 °C, depending on the surface orientation of the initial GaAs substrate. We note that the (001)GaAs substrate required the highest native oxide desorption temperature (680 °C).^{54,55} Moreover, the temperature referred to in this work is the thermocouple temperature. Additionally, *in situ* reflection high-energy electron diffraction (RHEED) was used to monitor the wafer surface during oxide desorption and throughout the epitaxy process. Following oxide desorption, a 200 nm-thick GaAs homoepitaxial buffer was grown on each GaAs substrate to create a smooth surface (*i.e.*, to reduce oxide desorption-induced surface roughening). The GaAs homoepitaxial buffers were grown at 500 °C, 550 °C, and 650 °C for the (111)A GaAs, (110)GaAs, and (001)GaAs substrates, respectively. A nominal GaAs growth rate of $\sim 1 \mu\text{m h}^{-1}$ was used throughout this work. After growth of the GaAs homoepitaxial buffer, each sample was cooled below 200 °C under a reducing As overpressure, and finally transferred to the Ge growth chamber for Ge epitaxy. The growth rate and growth temperature used during Ge epitaxy was $\sim 0.025 \mu\text{m h}^{-1}$ and 400 °C, respectively. Several Ge epilayer thicknesses were investigated (grown), after which the terminal Ge/GaAs heterostructure was slowly cooled to ~ 50 °C to mitigate thermal stresses in the heterostructure due to thermal expansion



coefficient mismatch between the epilayers. Further details regarding the growth process have been reported elsewhere.^{54,55} Moreover, as previously reported,^{56–58} the unintentional dopant (uid) concentration of these Ge epilayers fell in the range of $3 \times 10^{18} \text{ cm}^{-3}$ to $5 \times 10^{18} \text{ cm}^{-3}$ and exhibited electron-like conduction (n-type).

Additionally, a Cambridge NanoTech ALD reactor was utilized for the deposition of TaSiO_x on each crystallographically-oriented Ge/GaAs heterostructure, using the previously discussed Ta (tantalum(v) ethoxide, Ta(OEt)₅) and Si (tris(*tert*-butoxy)silanol, *t*BOS) precursors and a growth temperature of 250 °C. The steady-state ALD reactor background pressure prior-to and during deposition was ~150 mTorr. Each sample surface was treated with a standard solvent clean using acetone, isopropanol, and de-ionized water (DI H₂O), followed by a 60 s native oxide removal in a 10:1 buffered oxide etchant (HF) solution, prior to loading into the ALD reactor. Differing thicknesses of TaSiO_x (nominally 1.5 nm and 5 nm, see Section B for further details) were deposited using a Si precursor pre-pulsing stage followed by a Ta:Si super-cycle process, noting that DI water provided the oxygen source and N₂ (g) provided the purge gas. An initial *t*BOS/DI H₂O cycle was used to prime the sample surface (*i.e.*, pre-pulsing), followed by the 16 (3) Ta:Si super-cycles required for the 5 nm (1.5 nm) nominal TaSiO_x thickness. Each super-cycle consisted of one SiO₂ cycle per six Ta₂O₅ cycles, *i.e.*, 6:1 Ta:Si. Pulse times for the Ta and Si precursors were 0.020 s and 0.020 s, respectively, whereas the purge length was 5 s in between each pulse. Similarly, each DI H₂O pulse was 0.2 s. The approximate deposition rate following the conditions used herein was ~0.5 Å per cycle.

Following deposition of the TaSiO_x dielectrics, detailed XPS studies were performed in order to reveal the interfacial chemistry, oxide stoichiometry, and heterointerfacial energy band alignments of the crystallographically-oriented TaSiO_x/Ge heterostructures. A Phi Quantera Scanning XPS Microprobe equipped with a monochromatic Al-Kα (beam energy of 1486.7 eV) X-ray source was used in the XPS investigations, wherein the (photoelectron) exit angle used was 45°. A low-energy electron flood gun was used throughout spectral acquisition in order to neutralize positive charge accumulation on the oxide surface due to photoelectron generation (electron loss) during measurement. The C 1s core level (CL) binding energy (BE), nominally located at 285.0 eV, was used to correct the measured binding energies for each sample surface. Additionally, the O 1s spectra were recorded in order to determine the TaSiO_x bandgap (*via* the photoelectron energy loss technique, see Section B for further details) for each crystallographic orientation. Curve fitting was performed using CasaXPS v2.3.14, employing a Lorentzian convolution with a Shirley-type background for spectral fitting. Statistical deviation in the Au 4f_{7/2} CL BE of a Au standard was utilized in the derivation of a ±0.04 eV experimental uncertainty for this work, from which successive uncertainty was estimated using a root-sum-square approach. Lastly, cross-sectional transmission electron microscopy (X-TEM) was performed for the TaSiO_x/(001)Ge and TaSiO_x/(110)Ge heterostructures in order to elucidate the interfacial properties and

more-accurately determine the dielectric (and interfacial layer, if any) thickness(es). The TEM samples were prepared using conventional sample preparation methods, including mechanical polishing, dimpling, and low-temperature Ar⁺ ion milling.

Results and discussion

A. Oxide and interface chemistry: (Ta₂O₅)_{1-x}(SiO₂)_x *via* Ta:Si super-cycling during ALD

The composite (Ta₂O₅)_{1-x}(SiO₂)_x dielectric ALD process investigated herein was performed using *n*:*m* super-cycles, where “*n*” and “*m*” denote the number of Ta₂O₅/DI H₂O and SiO₂/DI H₂O cycles, respectively. Fig. 2 outlines the schematic process flow for each step involved in the deposition process of the (Ta₂O₅)_{1-x}(SiO₂)_x composite dielectric. Each Ta₂O₅/DI H₂O cycle consisted of one Ta(OEt)₅ pulse, followed by one DI H₂O pulse, with a short-duration N₂ purge separating each precursor pulse. Additionally, one cycle of *t*BOS pre-pulsing was used prior to the Ta:Si super-cycle process in order to study the efficacy of SiO_x interlayer formation on each Ge surface. Fig. 3a presents the first 100 s of a typical TaSiO_x ALD process, consisting of (i) the germinal *t*BOS/DI H₂O cycle used to saturate the Ge surface in an initiating Si/SiO_x layer, and (ii), a representative 6:1 Ta:Si super-cycle. This deposition process promoted the formation of an *in situ* interfacial SiO_x layer at the TaSiO_x/Ge interface.⁵⁰ Moreover, unlike the more thermodynamically stable and chemically robust native Si oxides, non-stoichiometric, easily-reduced native Ge oxides (*i.e.*, GeO_x) have been known to correlate to a high density of (potentially charged) interface states. Furthermore, the water solubility of native Ge oxides, in addition to their low κ value(s), frustrate the ability to effectively scale the equivalent oxide thickness (EOT) of composite dielectrics utilizing GeO_x (either native or intentionally re-grown) as an interfacial passivating layer (IPL). As such, the Si (or SiO_x) interlayer passivation technique has been suggested as a method to effectively passivate dangling Ge

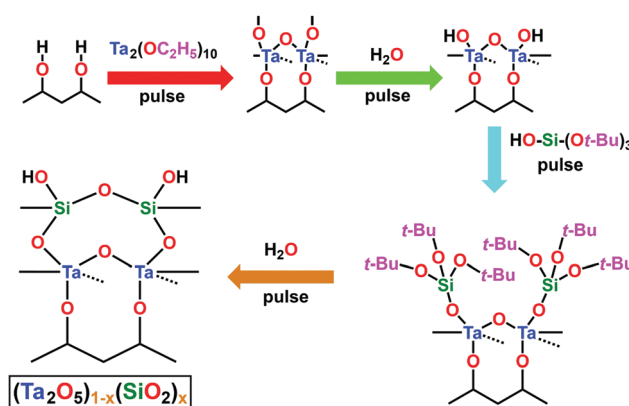


Fig. 2 Schematic representation of the process steps involved in the deposition of the composite dielectric, (Ta₂O₅)_{1-x}(SiO₂)_x. The depicted process flow begins subsequent to the pulsing of the Ta precursor, and prior to the pulsing of DI H₂O, which is the starting step in this diagram. The dashed lines represent the bond towards the back atom.



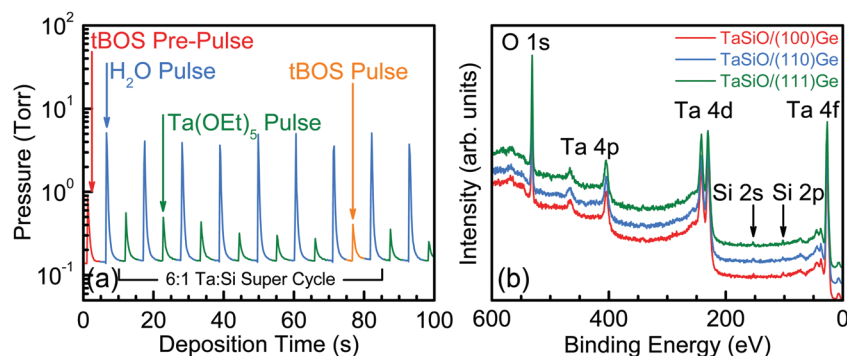


Fig. 3 (a) Representative TaSiO_x ALD process highlighting the initiating tBOS pulse as well as the 6 : 1 Ta : Si super cycle used in this work. (b) XPS survey spectra recorded from the surface of TaSiO_x as-deposited on (100)Ge (red), (110)Ge (blue), and (111)Ge (green) grown on GaAs. The position of the Si 2s and 2p spectral features indicate the incorporation of SiO₂ within the composite dielectric, (Ta₂O₅)_{1-x}(SiO₂)_x.

bonds (and therefore, available surface states), as well prevent subsequent oxidation of the Ge surface during dielectric deposition, and was studied herein.^{29,60–63}

In order to quantify the SiO_x incorporation rate within the composite (Ta₂O₅)_{1-x}(SiO₂)_x dielectric, XPS survey spectra were recorded for each crystallographically-oriented TaSiO_x/Ge heterostructure's surface, as shown in Fig. 3b. A 30 s, low-energy ($E \leq 1$ keV) Ar⁺ ion sputtering preceded spectral acquisition so as to remove residual surface contamination and minimize spurious extrinsic binding energy (BE) shifts. One can find from Fig. 3b that the Si 2p and Ta 4d_{5/2} BEs ($\sim 102.3 \pm 0.04$ eV and $\sim 229.7 \pm 0.04$ eV, respectively) correspond to those of the Si⁴⁺ and Ta⁵⁺ oxidation states (SiO₂ and Ta₂O₅, respectively), suggesting the stoichiometric formation of both constituent oxides during deposition. Moreover, utilizing the integrated photoelectron intensity for the Ta 4f, Si 2p, and O 1s spectral features, the concentration of SiO₂ within the as-deposited TaSiO_x composite dielectric was found to be 17.5%, in close agreement with the nominal (targeted) 20% SiO₂ composition.

A.1. Sputter depth-dependent XPS analysis of TaSiO_x dielectrics on epitaxial Ge. The SiO₂ incorporation uniformity was further investigated *via* XPS sputter depth profiling of the as-deposited TaSiO_x/(001)Ge specimen. Fig. 4 presents the Ta 4f and Ge 3d BE spectra as a function of sputter time for a nominally 5 nm TaSiO_x dielectric deposited on (001)Ge. Likewise, Fig. 4 show the Si 2p and O 1s BE spectra, respectively, of the

same. As shown in Fig. 4, an additional Ta 4f doublet appeared at the onset of sputtering and remain unchanged in BE throughout the entirety of the dielectric. The Ta 4f_{7/2} and Ta 4f_{5/2} BEs of the secondary doublet, 22.2 ± 0.04 eV and 24.05 ± 0.04 eV, respectively, corresponded to the metallic Ta bond (*i.e.*, Ta–Me). The consistency in BE position of the secondary doublet suggests that it was *not* a measurement artifact induced by preferential sputtering within the Ta₂O₅ constituent oxide.^{59–72} This conclusion was supported by previous work demonstrating negligible change in Ta₂O₅ stoichiometry due to Ar⁺ depth profiling; *i.e.*, within experimental error, the Ta₂O₅ was not reduced *via* low-energy ($E = 1.5$ keV) Ar⁺ ion bombardment.^{70,73} Besides, any such preferential sputtering would concomitantly and quantifiably alter the measured O 1s BE ($\sim 530.8 \pm 0.04$ eV), which was not observed in this work. Likewise, no quantifiable BE shift of the Si 2p spectra was observed as a function of sustained Ar⁺ sputtering, indicating that the Si–O bond (and not the Si–Me bond) remained the dominant Si bonding environment within TaSiO_x.

As such, the metallic Ta bond observed in Fig. 4 has two likely origins: (i) a persistent Ta–Ta bond that is relatively uniform throughout TaSiO_x; or (ii), an interaction between Ge and Ta atoms at the TaSiO_x/Ge interface, followed by the subsequent up-diffusion of the Ta–Ge bond. Although formation of Ta–Ta bonds cannot be ruled out during the deposition of TaSiO_x, their presence would imply (i) an incomplete Ta(OEt)₅–DI H₂O reaction, and/or (ii) the thermal decomposition of the

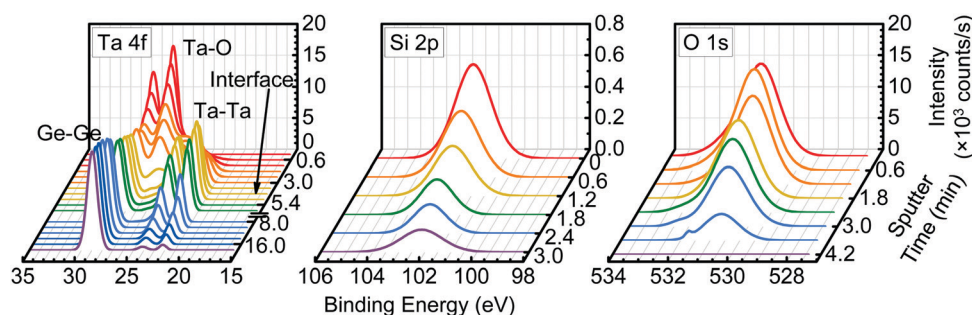


Fig. 4 XPS sputter depth profile of the as-deposited TaSiO_x/(100)Ge structure, consisting of the Ta 4f and Ge 3d (left), Si 2p (middle), and O 1s binding energy regions (right).

Ta(OEt)₅ precursor. However, in both scenarios, spectral features corresponding to residual hydrocarbons and Ta suboxides (e.g., Ta₂O₃[−]) would be expected in the recorded XPS spectra. Notably, neither of these distinct signifiers were observed herein. Consequently, we attribute the secondary Ta 4f doublet to the formation and diffusion of Ta–Ge bonds during the ALD of TaSiO_x.

Evidence for this conclusion can be found in Fig. 4, wherein the secondary Ta 4f doublet persisted in the metallic BE state beyond the point at which TaSiO_x had been wholly removed (sputtered) from the Ge surface. This point in time, 3.6 min < *t* ≤ 4.2 min, corresponded to the absence of the O 1s singlet in the measured XPS spectra, as shown in Fig. 4. The observation of the Ta 4f doublet in its metallic BE state for *t* > 4.2 min indicated the diffusion of Ta within Ge, and the increased likelihood for Ta–Ge bond formation. In the event that a single *t*BOS sub-cycle was insufficient to wholly encapsulate the Ge surface, the remaining OH-terminated Ge would have been partially exposed to an oxidation source in the form of DI H₂O (*g*). What is more, examining the standard Gibbs free energies of formation for Ta₂O₅ and GeO₂ reported in the literature, −1911 kJ mol^{−1} and −521 kJ mol^{−1} at 293 K, respectively,⁷⁴ one might expect preferential bonding of O with Ta at the TaSiO_x/Ge interface. We therefore posit that TaGe₂ formation at the non-Si(O_x)-encapsulated TaSiO_x/Ge interface, and subsequent up/down-diffusion enhanced by the formation of Ge–O, occurs during the ALD of TaSiO_x under the deposition conditions utilized herein.

Lastly, Fig. 5 presents the fitted Ta 4f_{5/2} and Si 2p peak intensities as a function of sputtering time, up to 3 min (*i.e.*, up to the loss of the Si 2p spectral feature). One can find from Fig. 5 that the fitted peak intensities of both the Ta 4f_{5/2} and Si 2p peaks decreasing monotonically with increased sputtering time, indicating: (i) a lack of preferential sputtering between the constituent Ta₂O₅ and SiO₂ oxides; and (ii) a uniform SiO₂ incorporation throughout the TaSiO_x composite dielectric.

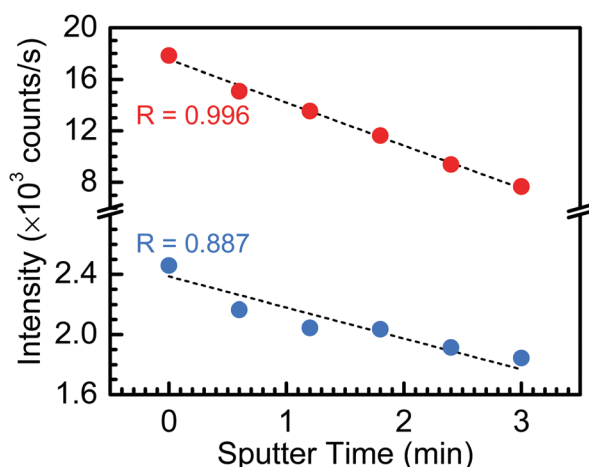


Fig. 5 Ta 4f and Si 2p core level binding energy peak intensities as a function of sputtering time, wherein the peak intensity of each constituent element (corresponding to the Ta₂O₅ and SiO₂ component oxides) decreases proportionally with increasing sputtering time.

A.2. TaSiO_x/Ge heterointerfacial characterization via TEM.

Fig. 6 shows the cross-sectional TEM micrographs of (a) TaSiO_x on (001)Ge/GaAs, (b) the epitaxial Ge/(110)GaAs heterointerface, and (c) TaSiO_x on (110)Ge/GaAs, respectively. The abrupt Ge-on-GaAs heterointerface, as observed in Fig. 6b, confirmed the high-quality Ge epitaxy. Furthermore, one can find from Fig. 6a and c that the TaSiO_x dielectric thickness was approximately 6.1 nm–6.2 nm, with an additional ~0.7 nm interfacial layer formed at the oxide/semiconductor interface due to the intentional *t*BOS/DI H₂O cycle provided prior to composite TaSiO_x deposition.⁵⁰ This is in good agreement with previous results investigating the integration of metal silicates on (001)In_xGa_{1−x}As and (110)In_xGa_{1−x}As thin-films, wherein an 8 Å (0.8 nm) SiO_x interfacial layer was observed at the oxide/semiconductor interface.⁴⁶ This suggests that no catalytic reaction between the Ta and Si precursors (Ta(OEt)₅ and *t*BOS, respectively) occurred for the deposition conditions used herein. Moreover, as evidenced by the sputter depth-dependent XPS analysis discussed earlier, it cannot be ruled out that the interfacial oxide also contains constituent GeO_x and TaO_x suboxides. If so, whereas a primarily SiO_x-based interlayer would increase the thermodynamic stability of the oxide/semiconductor heterointerface, one might expect that Ge- and Ta-suboxide incorporation would reduce interlayer robustness, even if it might (temporarily) passivate Ge dangling bonds at the Ge surface.^{29,30}

B. Energy band alignment properties of the TaSiO_x/Ge heterointerface

To evaluate the valence band discontinuity (ΔE_V) at the TaSiO_x dielectric/semiconductor interface, XPS spectra were recorded from: (i) nominally 5 nm (Ta₂O₅)_{1−x}(SiO₂)_x on crystallographically-oriented (001)Ge, (110)Ge, and (111)Ge, *i.e.*, “bulk-like” TaSiO_x; (ii) nominally 1.5 nm (Ta₂O₅)_{1−x}(SiO₂)_x on crystallographically-oriented (001)Ge, (110)Ge, and (111)Ge, *i.e.*, the oxide/semiconductor interface; and (iii), the surface of the as-grown (001)Ge, (110)Ge, and (111)Ge thin-films integrated on GaAs, *i.e.*, “bulk-like” Ge. Eqn (1), following the methodology developed by Kraut *et al.*⁷⁵ as utilized in previous studies,^{50,54,56,59,76–80} was used to determine the ΔE_V :

$$\Delta E_V = \left(E_{\text{Ta4d}_{5/2}}^{\text{TaSiO}_x} - E_{\text{VBM}}^{\text{TaSiO}_x} \right) - \left(E_{\text{Ge2p}_{3/2}}^{\text{Ge}} - E_{\text{VBM}}^{\text{Ge}} \right) - \left(E_{\text{Ta4d}_{5/2}}^{\text{TaSiO}_x} - E_{\text{Ge2p}_{3/2}}^{\text{Ge}} \right), \quad (1)$$

where $\left(E_{\text{Ta4d}_{5/2}}^{\text{TaSiO}_x(\text{Ge})} - E_{\text{VBM}}^{\text{TaSiO}_x(\text{Ge})} \right)$ is the BE separation between the Ta (Ge) 4d_{5/2} (2p_{3/2}) state and the VBM of the respective material and is the BE separation between the Ta 4d_{5/2} and Ge 2p_{3/2} states measured at the interface. Similarly, the conduction band offset (ΔE_C) can be determined using the following relation:

$$\Delta E_C = E_g^{\text{TaSiO}_x} - E_g^{\text{Ge}} - \Delta E_V, \quad (2)$$

where $E_g^{\text{TaSiO}_x}$ and E_g^{Ge} are the bandgaps of TaSiO_x and Ge, respectively, and ΔE_V is the measured valence band offset. Additionally, the bandgap (E_g) of the as-deposited TaSiO_x



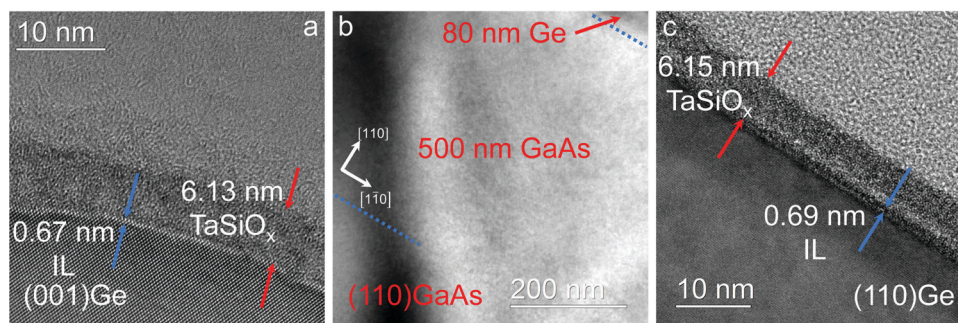


Fig. 6 Cross-sectional transmission electron micrographs showing the (a) TaSiO_x/(001)Ge heterointerface, (b) Ge epilayer as-grown on (110)GaAs using a 500 nm GaAs homoepitaxial buffer, and (c) the TaSiO_x/(110)Ge heterointerface. The interfacial SiO_x-based passivation layer is highlighted in each high-resolution micrograph.

dielectrics was determined for each crystallographic orientation utilizing the O 1s photoelectron energy loss spectra. Explicitly, the binding energy separation between the “onset” of photoelectron emission (with respect to the spectral background immediately following the O 1s peak) and the center of the fitted O 1s spectral feature(s) provides a direct method in determining an oxide’s bandgap. This is due to the nature of dielectric films, which require less energy for band-to-band excitation (*i.e.*, the lowest/principal valence and conduction bands) as opposed to plasmon losses.⁷⁰ A moderate range of bandgap values, between 4.4 eV–4.65 eV, have been reported in the literature, with variability in the measured bandgap stemming from the deposition method(s) utilized, or empirical method in determining the oxide bandgap (including XPS, photoluminescence and photoemission

spectroscopies) of Ta₂O₅.^{34–44} Cevro *et al.*³⁹ reported an optical bandgap varying from 4.3 eV–9.0 eV for $x = 1.0$ to $x = 0.0$ atomic mole fraction of Ta₂O₅ in the composite (Ta₂O₅)_{1-x}(SiO₂)_x dielectric. However, Adelmann *et al.*⁴⁰ found that for ALD TaSiO_x on Si, the bandgap starts to vary from ~ 4.5 eV for $x = 0.0$ up to ~ 4.9 eV for $x = 0.5$.⁴⁰ As such, a precise determination of the TaSiO_x E_g is important in order to accurately determine ΔE_C at the TaSiO_x/Ge heterointerface. Lastly, as discussed in the Experiments section, we note that statistical deviation in the Au 4f_{7/2} CL BE of a Au standard was utilized in the derivation of a ± 0.04 eV experimental uncertainty for this work, from which successive uncertainty was estimated using a root-sum-square approach.^{78–80}

B.1. Energy band alignment at the TaSiO_x/(001)Ge heterointerface. Fig. 7a shows the: (i) Ta 4d core-level (CL) BE and

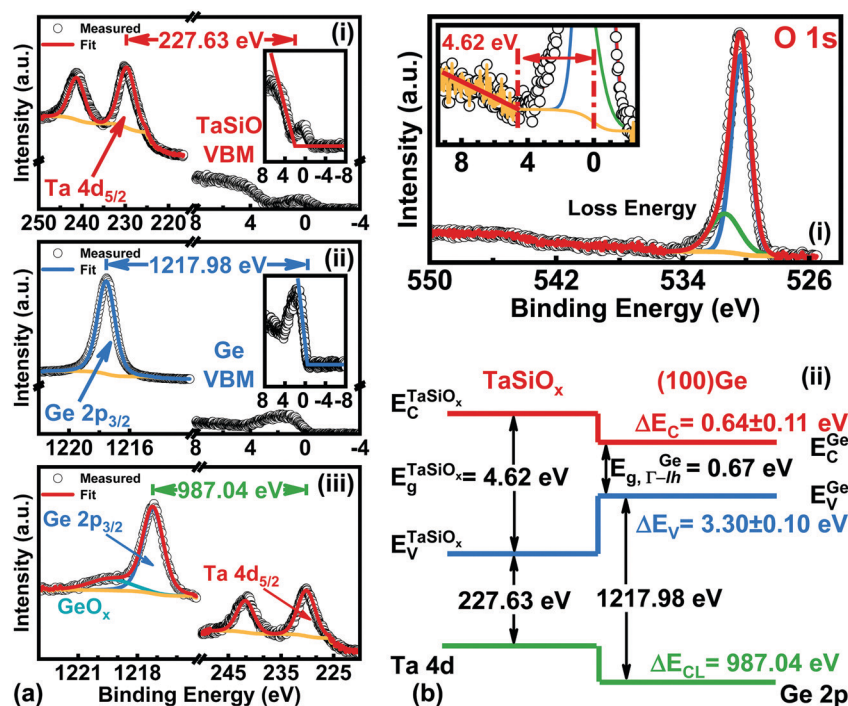


Fig. 7 XPS spectra of the: (a)(i) Ta 4d_{5/2} CL and VBM of “bulk-like” TaSiO_x deposited on (001)Ge/GaAs; (a)(ii) Ge 2p_{3/2} CL and VBM of “bulk-like” (001)Ge/GaAs; (a)(iii) Ta 4d_{5/2} and Ge 2p_{3/2} CLs recorded at the TaSiO_x/(001)Ge heterointerface; (b)(i) O 1s loss spectra used to extract the TaSiO_x bandgap (4.62 ± 0.06 eV); and (b.ii), the resulting band alignment at the TaSiO_x/(001)Ge oxide/semiconductor heterointerface.



valence band (VB) spectra recorded from the bulk-like TaSiO_x surface on (001)Ge; (ii) Ge 2p CL BE and VB spectra recorded from the bulk-like (001)Ge surface; and (iii), Ta 4d and Ge 2p CL BE spectra recorded at the TaSiO_x/(001)Ge interface. We note that the insets to Fig. 7a(i) and b(i) show the fitting of each material's VB spectra in order to determine their associated valence band maxima (VBM). Each VBM was determined by linearly fitting the onset of photoemission from the VB density of states with respect to the background photoemission. Similarly, Fig. 7b(i) shows the O 1s CL BE spectra recorded for the TaSiO_x/(001)Ge surface, from which a TaSiO_x $E_g = 4.62 \pm 0.06$ eV was determined following the procedures outlined earlier. Likewise, the measured BE separations between the samples shown in Fig. 7a were found to be: (i) 227.63 ± 0.06 eV; (ii) 1217.98 ± 0.06 eV; and (iii), 987.04 ± 0.06 eV. Substituting these BE separations into eqn (1), the empirical ΔE_V at the TaSiO_x/(001)Ge interface was determined, resulting in $\Delta E_V = 3.30 \pm 0.1$ eV, as shown in Fig. 7b(ii). Utilizing eqn (2), along with the measured TaSiO_x E_g and the literature-reported Ge bandgap ($E_g^{\text{Ge}} = 0.67$ eV, as measured between the *L*-valley conduction band minimum and the valence band maximum at the Γ point), ΔE_C was calculated to be 0.64 ± 0.11 eV. Table 1 summarizes the experimental energy band alignment parameters determined herein.

B.2. Energy band alignment at the TaSiO_x/(110)Ge hetero-interface. As demonstrated in Fig. 1, future Ge FinFET devices would utilize both (001)Ge and (110)Ge crystallographic orientations, with each surface orientation functioning as one (of three) MOS interfaces. As such, characterization of the crystallographic orientation-dependence of the TaSiO_x/Ge energy band alignment would provide vital guidance for device engineers seeking to utilize both material systems in future FET architectures. Correspondingly, and following the approach outlined in the preceding sections, ΔE_V and ΔE_C were determined at the TaSiO_x/(110)Ge heterointerface, employing eqn (1) and (2). Fig. 8a shows the: (i) Ta 4d CL BE and VB spectra recorded from the bulk-like TaSiO_x surface on (110)Ge; (ii) Ge 2p CL BE and VB spectra recorded from the bulk-like (110)Ge surface; and (iii), Ta 4d and Ge 2p CL BE spectra recorded at the TaSiO_x/(110)Ge interface. Likewise, Fig. 8b(i) shows the O 1s CL BE spectra recorded for the TaSiO_x/(110)Ge surface, from which a TaSiO_x $E_g = 4.66 \pm 0.06$ eV was determined. Using the measured BE separations highlighted in Fig. 8a, and the empirically-

determined TaSiO_x bandgap on the (110)Ge surface given above, ΔE_V and ΔE_C were found to be 3.36 ± 0.1 eV and 0.63 ± 0.11 eV, respectively, again using $E_g^{\text{Ge}} = 0.67$ eV, as shown in Fig. 8b(ii). As before, Table 1 provides all binding energy parameters used in the determination of the energy band offsets at the TaSiO_x/(110)Ge interface.

B.3. Energy band alignment at the TaSiO_x/(111)Ge hetero-interface. Fig. 9a shows the: (i) Ta 4d CL BE and VB spectra recorded from the bulk-like TaSiO_x surface on (111)Ge; (ii) Ge 2p CL BE and VB spectra recorded from the bulk-like (111)Ge surface; and (iii), Ta 4d and Ge 2p CL BE spectra recorded at the TaSiO_x/(111)Ge interface. Similarly, Fig. 9b(i) shows the O 1s CL BE spectra recorded for the TaSiO_x/(111)Ge surface, with a correspond TaSiO_x $E_g = 4.65 \pm 0.06$ eV. Combining the binding energy separation data presented in Fig. 9a, with the measured TaSiO_x/(111)Ge dielectric E_g , the empirical ΔE_V and ΔE_C at the TaSiO_x/(111)Ge interface were found to be 3.25 ± 0.1 eV and 0.73 ± 0.11 eV, respectively. These results, and their binding energy separation dependencies, are also presented in Table 1. Lastly, Fig. 10 summarizes the energy band alignment parameters for TaSiO_x on each crystallographic orientation for the Ge epilayers studied in this work. One can find from Fig. 10 (and Table 1) that ΔE_V was almost independent of the Ge surface orientation. Moreover, the relatively large ΔE_V values observed (as compared to ΔE_C) suggest improved hole confinement, broadly speaking, whereas the observed $\Delta E_C > 0.6 \pm 0.11$ eV would likely remain suitable for electron confinement under low voltage ($V_{\text{DD}} \leq 0.5$ V) operating conditions.

C. Surface chemistry at TaSiO_x/(001)Ge, (110)Ge, and (111)Ge heterointerfaces

The surface chemistry at the TaSiO_x composite dielectric/Ge heterointerface is important, as it is intrinsically linked to the electrical behavior of fabricated MOS devices.⁵⁸ One can find from Fig. 7a(iii), 8a(iii) and 9a(iii) that the sharp binding energy peak located at $\sim 1217.3 \pm 0.04$ eV, having a full-width at half-maximum (FWHM) of 1.25 eV–1.30 eV (± 0.04 eV), is characteristic of the Ge⁰ oxidation state, or simply put, the Ge–Ge bond attributable to the epitaxial Ge layer(s). On the other hand, the shoulder located at higher binding energy ($A_{\text{BE}} \sim 2.2 \pm 0.06$ eV), is indicative of the formation of an interfacial GeO_x transition region. It should be noted that such a GeO_x transition region was observed across all orientations. The conclusion that a GeO_x-containing transition region exists at the TaSiO_x/Ge interface is highlighted by the absence of a corresponding shoulder in the “bulk-like” Ge XPS spectra recorded from the Ge epilayer surface, as shown in Fig. 7a(ii), 8a(ii) and 9a(ii). One can find from Fig. 7a(ii), 8a(ii) and 9a(ii) that the “bulk-like” Ge XPS spectra (for each crystallographic orientation) were de-convolved into isolated Gaussian peaks corresponding to the Ge⁰ oxidation state (*i.e.*, the Ge–Ge metal bond) absent of any shoulder, indicating a lack of GeO_x on the surface of the as-grown Ge epilayer. It has already been shown that the ALD of Ta₂O₅ on Si results in an interfacial SiO₂ layer formed even at low deposition temperatures.⁴⁶ Moreover, given the pre-pulsing of TBOS prior to TaSiO_x ALD, and its resulting

Table 1 XPS-determined binding energy separations and corresponding energy band offset parameters for ALD amorphous TaSiO_x on epitaxial (001)Ge/GaAs, (110)Ge/GaAs, and (111)Ge/GaAs thin-films

Binding energy separation	(001)Ge	(110)Ge	(111)Ge
$E_{\text{Ge}2p_{3/2}}^{\text{Ge}} - E_{\text{VBM}}^{\text{Ge}}$	1217.98 ± 0.06	1217.94 ± 0.06	1217.92 ± 0.06
$E_{\text{Ta}4d_{5/2}}^{\text{TaSiO}_x} - E_{\text{VBM}}^{\text{TaSiO}_x}$	227.63 ± 0.06	227.51 ± 0.06	227.54 ± 0.06
$E_{\text{Ta}4d_{5/2}}^{\text{TaSiO}_x} - E_{\text{Ge}2d_{3/2}}^{\text{Ge}}$	-987.04 ± 0.06	-987.07 ± 0.06	-987.13 ± 0.06
ΔE_V (eV)	-3.30 ± 0.10	-3.36 ± 0.10	-3.25 ± 0.10
E_g of TaSiO _x (eV)	4.62 ± 0.06	4.66 ± 0.06	4.65 ± 0.06
ΔE_C (eV)	0.65 ± 0.11	0.63 ± 0.11	0.73 ± 0.11



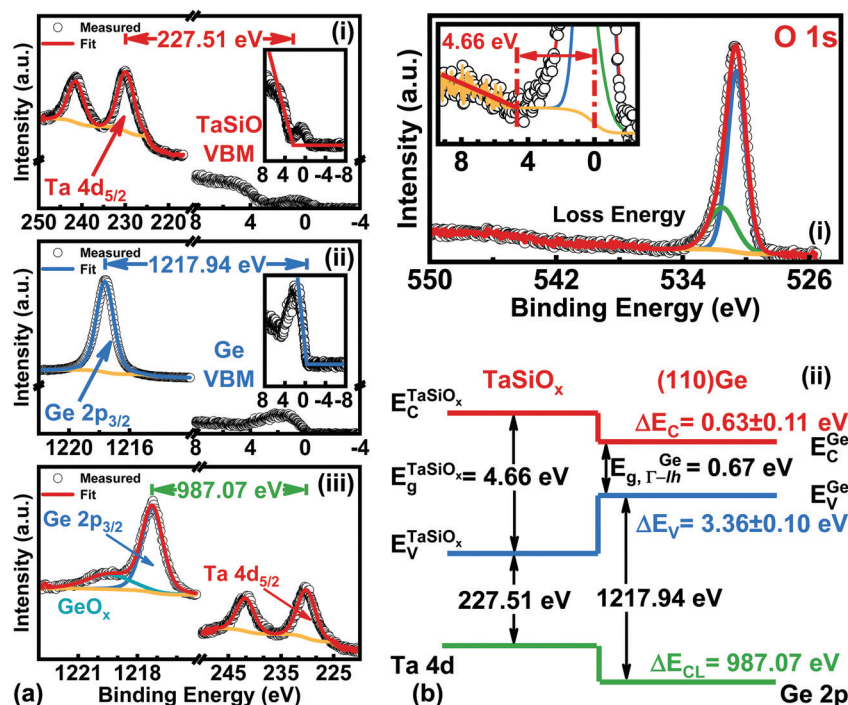


Fig. 8 XPS spectra of the: (a)(i) Ta 4d_{5/2} CL and VBM of "bulk-like" TaSiO_x deposited on (110)Ge/GaAs; (a)(ii) Ge 2p_{3/2} CL and VBM of "bulk-like" (110)Ge/GaAs; (a)(iii) Ta 4d_{5/2} and Ge 2p_{3/2} CLs recorded at the TaSiO_x/(110)Ge heterointerface; (b)(i) O 1s loss spectra used to extract the TaSiO_x bandgap (4.66 ± 0.06 eV); and (b)(ii), the resulting band alignment at the TaSiO_x/(110)Ge oxide/semiconductor heterointerface.

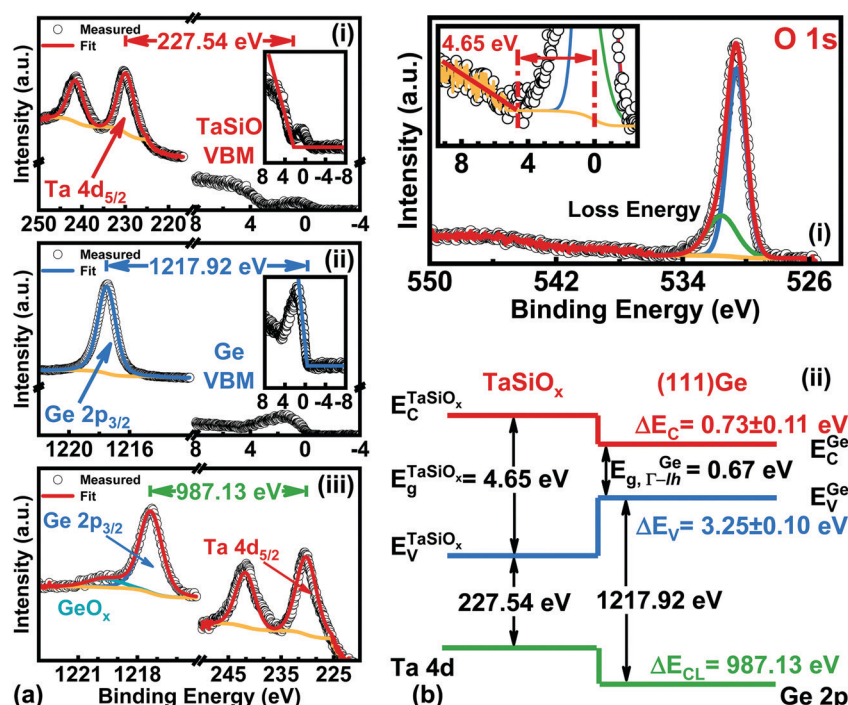


Fig. 9 XPS spectra of the: (a)(i) Ta 4d_{5/2} CL and VBM of "bulk-like" TaSiO_x deposited on (111)Ge/GaAs; (a)(ii) Ge 2p_{3/2} CL and VBM of "bulk-like" (111)Ge/GaAs; (a)(iii) Ta 4d_{5/2} and Ge 2p_{3/2} CLs recorded at the TaSiO_x/(111)Ge heterointerface; (b)(i) O 1s loss spectra used to extract the TaSiO_x bandgap (4.65 ± 0.06 eV); and (b)(ii), the resulting band alignment at the TaSiO_x/(111)Ge oxide/semiconductor heterointerface.

(intentional) ~7 Å interfacial layer formation, as demonstrated via TEM analysis, it is further possible that this interfacial

transition region consists of a complex, non-stoichiometric mixture of SiO_x, GeO_x, and TaO_x oxides/suboxides. Such a

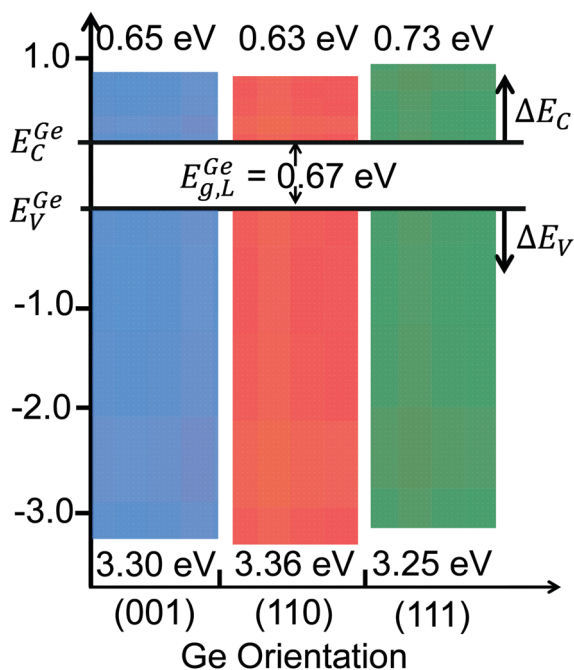


Fig. 10 Band offset distributions for TaSiO_x on the (001)Ge, (110)Ge, and (111)Ge surface orientations.

picture is consistent with the Ta and Ge diffusion mechanism posited in Section A.1, wherein exposure of the OH-terminated Ge surface (in regions not saturated by the TBOS precursor) to DI H₂O (g) would result in un-intentional oxidation of the Ge surface (as well as possible Ta–Ge bond formation). Such un-intentional GeO_x formation could likewise be exacerbated by diffusion of O downward, through the dielectric, and toward the interfacial oxide transition region. It is interesting to note that the width of this transition region, ~ 7 Å, mirrors that of similar TaSiO_x dielectric depositions performed (*via* ALD) on (nominally) In_{0.53}Ga_{0.47}As/(001) and (110)InP structures.⁵⁰

Lastly, Fig. 7b(i), 8b(i) and 9b(i) show the recorded O 1s spectra for each crystallographic orientation of Ge investigated in this work. As is evident from these figures, all O 1s spectral features were de-convolved into two Gaussian components – one peak exhibiting a narrow FWHM, and the other being a broad shoulder located at higher binding energy (relative to the former). The Gaussian peak located at lower binding energies ($\sim 530.5 \pm 0.04$ eV) is characteristic of the Ta⁵⁺ oxidation state in Ta₂O₅, which indicates the stoichiometric oxidation of Ta. The shoulder peak observed at higher binding energy ($\sim 531.5 \pm 0.04$ eV) was attributed to Ta–O–Si bonding, which was corroborated *via* Fig. 4 and 5 demonstrating the (uniform) incorporation of SiO₂ into the Ta₂O₅ matrix. Moreover, such SiO₂ incorporation could be expected to result in improved oxide thermal characteristics, such as increased recrystallization temperatures, as was observed in the case of HfSiO_x dielectrics. Too, the absence of suboxide formation in the bulk of the TaSiO_x dielectric is indicative of high-quality dielectric deposition.

Conclusions

In this work, (Ta₂O₅)_{1-x}(SiO₂)_x has been deposited by ALD, using Ta₂(O–C₂H₅)₁₀ and ((CH₃)₃CO)₃Si–OH for the Ta and Si precursors, respectively, on to crystallographically-oriented, epitaxial (001)Ge, (110)Ge, and (111)Ge thin-films grown on (001)GaAs, (110)GaAs, and (111)A GaAs substrates. Intentional pre-pulsing of the Si precursor (prior to composite TaSiO_x dielectric deposition) resulted in the formation of a SiO_x IPL at the dielectric/Ge interface, with the potential to passivate dangling bonds on the Ge surface, and thereby deleterious interfacial charge. Sputter depth-dependent XPS analysis through the TaSiO_x/Ge heterostructure revealed uniform Si incorporation throughout the composite TaSiO_x oxide, and a measurable degree of Ge and Ta atomic cross-diffusion across the oxide/semiconductor interface. Cross-sectional TEM analysis identified a distinct SiO_x IPL present on the Ge surface, likely originating in a complex, quaternary oxide structure (*i.e.*, that of GeO_x, SiO_x, and TaO_x) formed before and during the deposition of the overlying TaSiO_x oxide. Additionally, the bandgap of as-deposited, Ta-rich Ta_{0.8}Si_{0.2}O_x dielectrics was determined *via* XPS to be in the range of 4.62 eV–4.66 (± 0.06 eV), which was in excellent agreement with the bandgap values found in literature. The energy band discontinuities, *i.e.*, ΔE_V and ΔE_C , were found to be $> 3.0 \pm 0.1$ eV and $> 0.6 \pm 0.11$ eV, respectively, for all crystallographic orientations, which would suggest increased hole confinement across a wide operating voltage range, and sufficient electron confinement when operated at low drive voltages (*i.e.*, $V_{DD} < 0.5$ V). Moreover, the relatively high conduction and large valence band offsets observed in the TaSiO_x/Ge material system merits further investigation toward the development of Ge-based MOS devices for low- and ultra-low-power applications.

Author contributions

Michael Clavel: investigation, methodology, measurement, analysis, visualization, writing – review and editing; Shuvodip Bhattacharya: analysis, review and editing; Mantu Hudait: resources, supervision, project administration, funding acquisition, methodology, data curation, writing original draft, reviewing and editing.

Conflicts of interest

The authors declare no competing financial interests.

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