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Band alignment of vanadium oxide as an interlayer in a hafnium oxide-silicon gate stack structure

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Vanadium oxide (VO₂) is a narrow band gap material (Eg = 0.7 eV) with a thermally induced insulator-metal phase transition at \sim 343 K and evidence of an electric field induced transition at T < 343 K. To explore the electronic properties of VO₂, a sandwich structure was prepared with a 2 nm VO₂ layer embedded between an oxidized Si(100) surface and a 2 nm hafnium oxide (HfO₂) layer. The layer structure was confirmed with high resolution transmission electron microscopy. The electronic properties were characterized with x-ray and ultraviolet photoemission spectroscopy, and the band alignment was deduced on both *n*-type and *p*-type Si substrates. The valence band offset between VO₂ and SiO₂ is measured to be 4.0 eV. The valence band offset between HfO₂ and VO₂ is measured to be \sim 3.4 eV. The band relation developed from these results demonstrates the potential for charge storage and switching for the embedded VO₂ layer. © 2012 American Institute of *Physics*. [http://dx.doi.org/10.1063/1.4761990]

I. INTRODUCTION

Vanadium dioxide (VO₂) is a narrow band gap material (Eg = 0.7 eV).¹ The narrow band gap could enable vanadium dioxide films to act as charge storage sites if embedded in a gate stack structure.² Other studies have shown that vanadium dioxide nanostructures can be embedded in an oxide layer which can be considered for optical data storage.³ Vanadium dioxide displays an insulator to metal transition (IMT) at \sim 343 K with an abrupt three order of magnitude change of resistivity, which is typically accompanied by a structural phase transition.^{4–6} The other two common vanadium oxides, V_2O_3 and V_2O_5 , show IMT at 160 K^7 and 530 K, respectively.⁸ It has also been proposed that the application of an electric field to a VO2 film may increase the carrier density which could drive the transition to the metallic phase. This electric field induced phase transition could lead to a new class of electric switching devices,⁹ which could enable oxide based electronics.^{2,10} Recently, a UV photo induced phase transition of VO₂ has been studied using ultra fast pulsed laser spectroscopy and VO₂ nanodevices.^{11–14}

To develop efficient charge storage or switching devices based on the electronic properties of VO2, we need to understand the band alignment relative to dielectric interfaces and the Si substrate. In this study, we have prepared a thin VO₂ layer as an interlayer inserted between the adjoining high-k dielectric material (hafnium oxide (HfO₂)) and oxidized n- and p-type Si substrates. The layer structure was confirmed with high resolution transmission electron microscopy (TEM). The measurements on n- and p-type substrates explore charge transfer between the layers. HfO₂ is one of the most used high-k gate dielectric materials with a dielectric constant of 20-25 and band gap of 5.6 eV.¹⁵ In this structure, the VO_2 layer is able to accept charge through tunneling from the substrate. With the high-k upper layer, an applied gate voltage would control the potential of the VO₂ layer relative to the substrate. The band relations for HfO_2 , VO_2 , and the oxidized *n*- and *p*-type Si substrate are determined from *in-situ* photoemission measurements, and the interfacial charge transfer during the growth is discussed.

II. EXPERIMENT

The experiments were accomplished *in-situ* using an integrated ultrahigh vacuum (UHV) system. This system involves a linear $\sim 20 \text{ m}$ UHV transfer line chamber with a base pressure of 5×10^{-10} Torr that connects different processes and characterization chambers. In this study, the following systems are used: remote oxygen plasma for cleaning, reactive electron beam deposition system for HfO₂ and VO₂ growth, x-ray photoelectron spectroscopy (XPS) for core level analysis, and ultraviolet photoelectron spectroscopy (UPS) for valence band spectra.

The samples are grown on 25 mm diameter *n*-type, phosphorous doped, (100) silicon wafers with a resistivity of 0.05-0.09 Ω ·cm and *p*-type, boron doped, (100) silicon wafers with resistivity of 0.006-0.01 Ω ·cm. Before loading into the UHV chamber, wafers are cleaned in an ultrasonic acetone bath for 15 min, an ultrasonic methanol bath for another 15 min, and dried in ultra high purity nitrogen gas. After transfer into the UHV system, the Si(100) surfaces are cleaned and oxidized by a remote oxygen plasma. The plasma exposure conditions are as follows: substrate at room temperature, 60 mTorr oxygen pressure, gas flow of 10 standard cubic centimeters per minute (sccm), and rf power of 30 W to excite the plasma. The remote oxygen plasma can effectively remove hydrocarbon contamination and passivate the Si surface with a thin SiO₂ layer.¹⁶ After *in situ* cleaning, the sample was annealed at 500 °C for 5 min. for defect reduction and removal of adsorbed oxygen. The surfaces were then characterized by XPS and UPS.

The VO₂ and HfO₂ films were deposited in the reactive electron beam deposition system which has a base pressure of 7×10^{-9} Torr. The electron beam crucibles were filled with 99.8% vanadium and 99.9% hafnium metals. A 2 nm thick VO₂ film was deposited onto the cleaned Si wafer at

550 °C with an oxygen gas pressure of 6×10^{-4} Torr. Prior to the interface study described here, the growth conditions were established by preparing ~50-100 nm thick VO₂ films deposited on both silicon and sapphire substrates. XPS and RBS measurements of these films indicated a V to O atomic ratio of 1:2 within 5%. The resistance of the VO₂ films changed by ~2 orders of magnitude as the temperature increased from room temperature to 100 °C showing results consistent with prior reports. Another 2 nm HfO₂ film was directly deposited over the VO₂ layer at room temperature with an oxygen pressure of 2×10^{-6} Torr. For each layer, a growth rate of 0.01 nm/s was maintained with a quartz crystal thickness rate meter.

The sample was characterized by XPS and UPS at each step. XPS characterization is performed at a base pressure of 6×10^{-10} Torr using the 1253.6 eV Mg K α line of a VG XR3E2 dual anode source and a VG microtech Clam II analyzer operated at a resolution of 0.1 eV. The resolution of the analyzer was determined from the full width at half maximum (FWHM) of a gold 4f 7/2 spectral peak to be approximately 1.0 eV; however, through curve fitting, the centroid of spectral peaks can be resolved to $\pm 0.1 \,\text{eV}$. Ultraviolet photoemission spectra are obtained at a base pressure of 8×10^{-10} Torr using the He I line at 21.2 eV and a VSW 50 mm mean radius hemispherical analyzer and VSW HAC 300 controller operated at an electron energy resolution of 0.15 eV. A negative 4.00 V bias was applied to the substrate to overcome the work function of the analyzer. A representative sample was observed in cross-section geometry using a JEOL JEM 4000EX high-resolution electron microscope operated at 400 kV.

III. RESULTS

The *in situ* experiments consisted of the following process: (1) remote oxygen plasma cleaning, (2) XPS and UPS characterization, (3) deposition of $\sim 2 \text{ nm}$ vanadium oxide, (4) XPS and UPS characterization, (5) deposition of $\sim 2 \text{ nm}$ of hafnium oxide, (6) XPS and UPS characterization. The results of XPS and UPS spectra of each step are shown in Figs. 1–4. The XPS observation "windows" were set for the Si 2p, O 1s, V 2p, and Hf 4f core levels. The carbon XPS peaks were below the detection limit before and after deposition.

A. Si substrate with native oxide layer

The Si 2p core level is shown in Fig. 1. The initial SiO₂ layer thickness can be determined from the ratio of the bulk (~99 eV) and SiO₂ (~104 eV) Si peaks. The SiO₂ thickness was determined using the following equation:¹⁷ t_{ox} = λ_{SiO2} ln {[(1/ β) (I_{SiO2}^{exp}/I_{Si}^{exp})] + 1}, where λ_{SiO2} is the attenuation length of the Si 2p photoelectrons in SiO₂, β = (I_{SiO2}^{∞}/I_{Si}^{∞}) is the ratio of the Si 2p intensity from thick SiO₂ and a Si wafer, and I_{SiO2}^{exp}/I_{Si}^{exp} is the measured ratio of normal incident XPS Si 2p intensities. For our XPS instrument configuration, the analyzer is normal to the sample. We take λ_{SiO2} to be 2.8 ± 0.02 nm, an average from five references, ^{18–22} and β to be 0.83.²² With these values and the measured intensities



FIG. 1. X-ray photoemission spectra of Si 2p peaks for (a) plasma oxidized n-type Si(100) and (b) p-type Si(100) sample. The curves are for the oxidized Si wafer, after deposition of VO₂ on Si and after deposition of HfO₂.

ratio, the thickness of the initial SiO₂ layer on the Si wafer is determined to be 0.8 ± 0.1 nm.

For the *n*-type sample, the XPS binding energies of the Si 2p, O 1s, V 2p3/2, and Hf 4f 7/2 are summarized in Table I. The initial Si 2p peaks are at 99.7 and 103.6 eV, respectively, corresponding to bulk Si near the surface and the SiO₂ layer of the oxidized Si. Results have established that the Si 2p core level is 98.8 eV below the valence band maximum (VBM).²³ For the heavily doped *n*-type Si wafer, the Fermi level is at 0.9-1.0 eV above the VBM. Therefore, the initial *n*-type Si substrate displays a flat band condition as the Si 2p peak is at 99.7 eV (98.8 + 0.9 eV). After VO₂ deposition, the Si bulk and SiO₂ related peaks are shifted to lower binding energies of 99.4 and 103.0 eV, respectively. After 2 nm HfO₂ deposition, the Si peaks shift back to 99.6 and 103.2 eV, respectively. The shifts in the Si bulk feature are attributed to a change of the band bending in the Si substrate, and the differential shifts between the Si substrate and Si oxide features are attributed to an electric potential across the SiO₂ layer.

For the *p*-type sample, the XPS binding energies of the Si 2p, O 1s, V 2p3/2, and Hf 4f 7/2 core levels are



FIG. 2. X-ray photoemission spectra of O 1s and V 2p peaks for (a) plasma oxidized *n*-type Si(100), (b) vanadium oxide on oxidized *n*-type Si(100), and (c) HfO₂ and VO₂ on oxidized *n*-type Si(100). The figure inset shows the O1s curve fitting peaks for 2 nm HfO₂ on *n*-type and *p*-type Si.

summarized in Table II. The bulk Si 2p peak is at 99.0 eV. Assuming that the Fermi level is 0.1 eV above the VBM for the heavily doped *p*-type Si wafer, and the Si 2p core level is 98.8 eV below the VBM, the results indicate the initial *p*-type Si substrate is at a flat band condition.

After VO₂ deposition, the Si bulk and SiO₂ related peaks are shifted to lower binding energies of 99.0 eV and 102.6 eV, respectively. After 2.0 nm HfO₂ deposition, the Si bulk and SiO₂ related 2p peaks shift to higher binding energies of 99.1 and 103.2, respectively.

B. 2 nm VO₂

The O 1s and V 2p core levels are shown in Fig. 2. For the *n*-type substrate, the peak at 532.6 eV is the O 1 s signal of the oxygen in the SiO₂ layer. After VO₂ deposition, the peak at 530.6 eV is attributed to the O 1s signal corresponding to the VO₂ layer. Also, a shoulder peak at the left-hand side of the 530.6 eV peak is attributed to the O 1s in the SiO₂ layer. This shoulder peak is located at 532.0 eV, which is 0.6 eV lower than the initial state. This shift is consistent with the shift of the Si peak in the SiO₂ layer which is also 0.6 eV lower after VO₂ deposition. After the HfO₂ capping



FIG. 3. X-ray photoemission spectra of Hf 4f peaks for HfO_2 and VO_2 on (a) oxidized *n*-type Si(100) substrate and (b) *p*-type Si(100) substrate.

layer, the O 1s peak is mostly due to oxygen in the HfO₂. After the initial 2.0 nm VO₂ deposition, the V 2p3/2 peak is located at 516.0 eV. After the HfO₂ deposition, the V 2p3/2 peak is shifted to a lower binding energy of 515.6 eV, which may be due to the extraction of oxygen from the VO₂ layer during HfO₂ deposition. The V 2p3/2 peak at 513.3 eV may be due to other vanadium oxides²⁴ or vanadium-hafnium interface oxides.

For the *p*-type substrate, (Fig. 2(b)), the peak at 532.2 eV is the O 1s signal of the oxygen in the SiO₂ layer. After VO₂ deposition, the peak at 529.9 eV is attributed to the O 1s signal of oxygen in the VO₂ layer. Also, a shoulder peak at the lefthand side of the 531.6 eV peak is attributed to the O 1s from the SiO₂ layer. This shoulder peak is located at 531.6 eV, which is 0.6 eV lower than the initial state. This shift is comparable with the Si peak shift in the SiO₂ layer which is also 0.6 eV lower after VO₂ deposition. The V 2p3/2 peak is located at 516.2 eV. After the 2.0 nm HfO₂ layer deposition, the intensity of the V 2p3/2 peak due to VO₂ is significantly decreased. Again, a peak located around 513.5 eV is detected, which may be other vanadium oxides or a vanadium-hafnium complex oxide. The main O1s peak, located at 530.8 eV after the



FIG. 4. Ultraviolet photoemission spectra of (a) plasma oxidized *n*-type Si(100), (b) vanadium oxide on oxidized *n*-type Si(100), and (c) HfO₂ and VO₂ on oxidized *n*-type Si(100).

the 2.0 nm HfO_2 capping layer, represents the oxygen signal from the HfO_2 layer.

C. 2 nm HfO₂

Fig. 3 presents the Hf XPS 4f peaks as evidence of the HfO_2 layer. For the 2.0 nm HfO_2 layer on *n*-type Si, the Hf 4f 7/2 and 4f 5/2 peaks are located at 17.9 and 19.4 eV, respectively. For the 2.0 nm HfO_2 layer on *p*-type Si, the Hf 4f 7/2 and 4f 5/2 peaks are located at 17.9 and 19.4 eV, respectively.

TABLE I. XPS Si 2p, O1s, V2p 3/2, and Hf 4f 7/2 core level results for $HfO_2/VO_2/oxidized n$ -type Si(100). Values have an uncertainty of $\pm 0.1 \text{ eV}$.

<i>n</i> -sample	Si 2p (eV)		O 1s (eV)			
Process	Si bulk	SiO ₂	Main	Shoulder	V 2p3/2 (eV)	Hf 4f7/2 (eV)
Substrate	99.7	103.6	532.6			
2nm VO_2	99.4	103.0	530.6	532.0 (SiO ₂)	516.0	
2 nm HfO ₂	99.6	103.2	530.9	530.3 (VO ₂)	515.6	17.9

TABLE II. XPS Si 2p, O1s, V2p 3/2, and Hf 4f 7/2 core level results for $HfO_2/VO_2/oxidized p$ -type Si(100). Values have an uncertainty of $\pm 0.1 \text{ eV}$.

<i>p</i> -sample	Si 2p (eV)		O 1s (eV)			
Process	Si bulk	SiO ₂	Main	Shoulder	V 2p3/2 (eV)	Hf 4f7/2 (eV)
Substrate	99.0	103.2	532.2			
2 nm VO_2	99.0	102.6	529.9	531.6 (SiO ₂)	516.2	
2 nm HfO ₂	99.1	103.2	530.8	529.7 (VO ₂)		17.9

D. Ultraviolet photoemission spectra

The ultraviolet photoemission spectra of the cleaned, oxidized substrate, after VO2 deposition, and after HfO2 deposition for both *n*- and *p*-type substrates are shown in Fig. 4. The UPS spectrum of the initial clean SiO_2 layer on *n*-type and p-type Si substrates shows the VBM at 5.5 eV and 5.0 eV below the Fermi level. The valence band offset between Si and SiO₂ is then $4.5 \,\mathrm{eV}$ for the *n*-type Si substrate, which agrees with previous results for the Si-SiO₂ band offset.²⁵ These results are consistent with a low interface state density and negligible band bending for the *n*-type substrate. For the *p*-type substrate, there is an $\sim 0.4 \text{ eV}$ inconsistency between the XPS and UPS results for the determination of the VBM of the SiO₂. Given the sensitivity of UPS measurements, we have used the XPS results to determine the relative band positions for the SiO₂. For the VO₂ film, the V 3d peak is close to the Fermi level, and the cutoff of this peak gives the valence band maximum at 0.6 eV below the Fermi level for both *n*- and *p*-type substrates, respectively. The results indicate that the material is in the insulating phase as anticipated. While intense pulsed UV laser light between 0.8 and 3 eV has been shown to induce the insulator-metal phase transition, ^{11–14} the low intensity of the photoemission UV light source is insufficient to induce the phase change. Previous photoemission measurements of the VO₂ IMT also support this conclusion.²⁶ After the 2.0 nm HfO₂ layer deposition, the front cutoff of the UPS spectra indicates the valence band maximum relative to the Fermi level at 4.0 eV for both of the *n*-type and *p*-type sample.

E. Transmission electron microscopy

Figure 5 displays a cross-sectional electron micrograph of the *n*-type sample structure. The VO₂ and HfO₂ layers are \sim 1.6 nm and 1.9 nm in thickness, respectively. The final SiO₂ layer is \sim 1.3 nm suggesting that the thickness increased due to substrate oxidation during the higher temperature growth of the VO₂ layer. This is also consistent with the XPS results. From Fig. 1, the ratio $(I_{SiO2}^{exp}/I_{Si}^{exp})$ of XPS intensities is calculated as 26% for the initial oxidized n-type substrate which increases to 41% for the final *n*-type sample. The corresponding values are 21% for the initial oxidized p-type substrate which increases to 73% for the final p-type sample. Both results indicate that the SiO₂ layer became thicker after deposition of the oxide layers. There is no evidence of crystalline order or domains in any of the oxide layers. The contrast of each oxide layer is uniform and changes sharply at the Si/SiO2, SiO2/VO2, and VO2/HfO2



FIG. 5. Cross sectional TEM image of the $HfO_2/VO_2/SiO_2$ structure on *n*-type Si. A Pt capping layer was employed to protect the surfaces during specimen preparation.

interfaces. The results indicate an amorphous structure and sharp interfaces without evidence of intermixing.

IV. DISCUSSION

A. Valence band offset

In our study, we employ UPS to determine the VBM and XPS to measure the core level energies both with respect to the Fermi energy. For the *p*-type sample, we adopt the value derived from XPS data for the initial band conditions. The valence band offset (VBO) of VO₂ and SiO₂ can be expressed in method (1) as follows:

$$VBO = E_{VBM}{}^{SiO2} - E_{VBM}{}^{VO2} - \Delta^{Si} - \Delta^{SiO2}, \quad (1)$$

where E_{VBM}^{SiO2} and E_{VBM}^{VO2} are the VBM (relative to the Fermi level) of the initial clean oxidized Si substrate (SiO₂ layer) and the VO₂ layer obtained by UPS, respectively. The Δ^{Si} is the change of band bending of the Si substrate, and Δ^{SiO2} is the change of electric potential across the SiO₂ layer both after VO₂ layer deposition. From Eq. (1) and Table III(a), the VBO of VO₂/SiO₂ is calculated as $4.0 \pm 0.1 \text{ eV}$ and $4.0 \pm 0.1 \text{ eV}$ for films on the *n*- and *p*-type Si substrate, respectively.

The VBO of VO_2 and SiO_2 can also be expressed in method (2) as follows:

$$VBO = (E_{2p3/2}{}^{VO2} - E_{VBM}{}^{VO2}) - (E_{2p}{}^{SiO2} - E_{VBM}{}^{SiO2}) - \Delta 1 (E_{2p3/2}{}^{VO2} - E_{2p}{}^{SiO2}) - \Delta 2 (SiO_2),$$
(2)

where $(E_{2p3/2}^{VO2} - E_{VBM}^{VO2})$ is the V 2p3/2 core level to VBM of VO₂, $(E_{2p}^{SiO2} - E_{VBM}^{SiO2})$ is the Si 2p core level to VBM of SiO₂, $\Delta 1(E_{2p3/2}^{VO2} - E_{2p}^{SiO2})$ is the energy separation between the V 2p3/2 of VO₂ and Si 2p of SiO₂, and $\Delta 2(SiO_2)$ is the electrical potential across the SiO₂ layer. From Eq. (2) and Table III(b), the VBO of VO₂/SiO₂ is calculated as 4.0 and 4.0 eV for the *n*-type and *p*-type Si

TABLE III. Tabulated electronic structure for VO₂ on Si substrate, including (a) VBM of SiO₂ and VO₂, the change of band bending (Δ^{Si}), the electrical potential change on SiO₂ layer (Δ^{SiO2}), and VBO, (b) V 2p3/2 core level to VBM of VO₂ ($E_{2p3/2}^{VO2} - E_{VBM}^{VO2}$), Si 2p core level to VBM of SiO₂ ($E_{2p}^{SiO2} - E_{VBM}^{SiO2}$), energy separation between V 2p3/2 of VO₂ and Si 2p of SiO₂ (Δ 1), and electrical potential change from the mid of SiO₂ layer to the interface of VO₂/SiO₂, (Δ 2). For the *p*-type sample, we adopt the value derived from XPS data for the initial band conditions.

(a)	VBM $SiO_2(eV)$	VBM VO ₂ (eV)	$\Delta^{Si}\left(eV\right)$	$\Delta^{SiO2}\left(eV\right)$	VBO (eV)	
<i>n</i> -type	5.5	0.6	0.3	0.6	4.0	
<i>p</i> -type	4.6	0.6	0.0	0.0	4.0	
(b)		<i>n</i> -ty	pe	<i>p</i> -type		
(E _{2p3/2}	$VO2 - E_{VBM} VO2$) (eV) 515.4 (516	.0 - 0.6)	515.6 (51	6.2 - 0.6)	
(E _{2p} SiO	$^2 - E_{VBM}^{SiO2}$) (eV	/) 98.1 (103.	6 – 5.5)	98.6 (103	3.2 - 4.6)	
$\Delta 1 (E_{2p3/2}VO_2)$		413.0 (516.0	413.0 (516.0 - 103.0)		413.0 (516.2 - 103.2)	
$-E_{2p}S$	iO_2) (eV)					
$\Delta 2 (SiO_2) (eV)$		0.3	0.3		0.0	
VBO (eV)		4.0)	4.0		

substrates, respectively. The values of the VBO of VO_2/SiO_2 calculated from the two methods are then consistent.

The interfacial dipole is calculated as the difference between the vacuum levels of the two adjoining materials, which can be expressed as follows:

$$\Delta \text{Dipole} = (hv - W^{\text{SiO2}}) - (hv - W^{\text{VO2}}) - VBO^{\text{SiO2/VO2}}$$
$$= W^{\text{VO2}} - W^{\text{SiO2}} - VBO^{\text{SiO2/VO2}}$$

where hv = 21.2 eV is the He I photon energy, W represents the width of UPS spectra, for SiO₂ as 11.7 eV, VO₂ as 15.6 eV, and HfO₂ as 13.4 eV from the *n*-type sample measurements, respectively. Because the spectra for the *n*-type sample were of high quality at both the low and high energy cutoffs, these values have been adopted for both the n- and *p*-type samples. Here (hv - W) is the energy of the vacuum level relative to the VBM and $VBO^{SiO2/VO2}$ is the SiO₂/VO₂ valence band offset. The VO_2/SiO_2 interfacial dipole can be calculated as 0.1 eV on the n- and p-type Si substrate. Similarly, The HfO₂/VO₂ interfacial dipole can be calculated as 1.2 eV on the *n*-type Si substrate and 1.1 eV on the *p*-type Si substrate. This indicates the electron affinity model only describes the band offset of the VO₂/SiO₂ interface well, indicating a small interfacial dipole, but it is less consistent for the whole HfO₂/VO₂/SiO₂/Si bands.

Robertson²⁷ has developed a model which presumes that the charge will transfer and align the charge neutrality levels (CNL) at the interface. The CNL of HfO₂ as calculated by local density approximation (LDA) is 3.7 eV and the CNL of SiO₂ is calculated as 4.5 eV.^{28} According to the CNL model, the valence band offset of HfO₂/SiO₂ is expected to be 0.8 eV without a VO₂ interlayer. Considering the valence band offset of VO₂/SiO₂ is measured as 4.0 eV, the valence band offset of HfO₂/VO₂ is predicted as 3.2 eV by the CNL model. Our results show that for the *n*-type and *p*-type substrate, the VBM of HfO₂ is 4.0 eV, and the VBM of VO₂ is 0.6 eV. The valence band offset for HfO₂/VO₂ is determined as 3.4 eV, which is comparable to the predicted 3.2 eV value. We consider now the relative band alignment of HfO₂ on SiO₂ on Si without and with the VO₂ inter-layer. The valence band offset of HfO₂/SiO₂ from previous experimental results was found to be $1.05 \pm 0.1 \text{ eV}^{.29}$ In this study, the relative band offset of the HfO₂/SiO₂ with the VO₂ interlayer is found to be 0.8 eV for the *n*-type substrate and 0.6 eV for the *p*-type substrate. Thus, it appears that both the VO₂/SiO₂ and HfO₂/VO₂ interfaces have the same origin of the interface dipole. Robertson has noted that the CNL model would predict a VBO of 0.8 eV for HfO₂/SiO₂ without a VO₂ interlayer. This result indicates that the CNL model describes the band offset of the HfO₂/VO₂/Si substrate system.

B. Band alignment schematics

Fig. 6 shows diagrams of the band alignment for the different stages of development of the *n*-type sample structure. According to the XPS and UPS analysis, the band bending at the SiO₂/Si interface is less than the 0.1 eV resolution limit of the measurement, which indicates the substrate is at a flat band condition. Assuming the 0.1 eV value as a limit, the interface charge density is less than $3.6 \times 10^{11} \text{ cm}^{-2}$. Considering the 1.1 eV band gap of Si and the 8.9 eV band gap of SiO₂, the conduction band alignment for the oxidized *n*-type Si substrate is also shown in Fig. 6(a). After deposition of the 2 nm VO_2 layer, the bulk Si core level shifts to lower binding energy by $\sim 0.3 \,\text{eV}$, indicating upwards band bending. The Si core level in the SiO₂ layer shifts to lower binding energy by $\sim 0.6 \,\mathrm{eV}$, indicating an electric potential across the SiO₂ layer. Subtracting the Si core level shift (band bending), the potential across the SiO₂ layer is 0.6 V (2 × (0.6 - 0.3) V). Using 0.8 nm for the thickness of the SiO₂, the electric field across the SiO₂ layer is 7.5×10^8 V/m. It is presumed that there is no significant electric field across the low band gap vanadium oxide layer. According to the UPS results, the VBM of VO₂ is 0.6 eV below the Fermi level. Since this thin and amorphous VO₂ film may have larger band gap than 0.7 eV, the conduction band minimum (CBM) is indicated as a dashed line at 0.7 eV above the valence band. The band alignment of the two oxide layer structure is shown in Fig. 6(b). It is noted that the CBM for all of the oxides is deduced from the reported values of the band gap, and the CBM is shown as dashed lines in the figures. After deposition of the 2 nm HfO₂ layer, the Si 2p peaks of the Si and SiO₂ shift back to 99.6 eV and 103.2 eV, respectively. A slight upwards band bending is indicated for the Si wafer, and the potential across the SiO₂ is 0.6 V. The V 2p3/2 peak shifts from 516.0 to 515.6 eV, an ~0.4 eV shift. According to the UPS results, the VBM of HfO₂ is 4.0 eV below the Fermi level. Considering the VBM of VO₂ at 0.6 eV below the Fermi level and assuming a negligable field across the VO₂ layer, the VBO of HfO₂/VO₂ is determined as 3.4 eV. Considering the band gap of HfO₂ as 5.7 eV, the band alignment of the final structure is shown in Fig. 6(c).

Fig. 7 shows the band alignment diagrams for the different stages of development of the *p*-type sample structure. Considering the 1.1 eV band gap of Si, the 8.9 eV band gap of SiO₂ and the 4.5 eV band offset at the Si/SiO₂ interface, the band alignment for the oxidized p-type Si substrate are shown in Fig. 7(a). According to the XPS data analysis, the oxidized *p*-type Si substrate is at a flat band condition. After deposition of the 2 nm VO₂ layer, the bulk Si core level at the SiO₂/Si interface remains at the same position as the oxidized Si substrate. In this case, after the VO₂ deposition, the Si substrate is still at a flat band condition. Again, it is also presumed that there is no significant electric field across the vanadium oxide layer. According to the UPS results, the VBM of VO₂ is 0.6 eV below the Fermi level. The band alignment of these two oxide layers is shown in Fig. 7(b). After deposition of the 2 nm HfO₂ layer, the bulk Si core level at the SiO₂/Si interface and the Si core level of the SiO₂ shift to higher binding energies of 99.1 eV and 103.2 eV, respectively. Considering the 0.1 eV uncertainty, the substrate remains at the initial flat band condition. According to the UPS results, the VBM of HfO₂ is 4.0 eV below the Fermi level. Considering the VBM of VO₂ at 0.6 eV below Fermi level and assuming a negligible field across the VO₂ layer, the VBO of HfO₂/VO₂ is determined as 3.4 eV. The band alignment of the final structure is shown in Fig. 7(c). The small difference of the interface band offsets is most likely due to experimental uncertainties.

The results show the development of the band alignment for the HfO_2 , VO_2 , and oxidized Si substrate. The major difference between the structures on *p*- and *n*-type Si substrates



FIG. 6. Band alignment of (a) plasma oxidized *n*-type Si(100), (b) VO₂ on oxidized *n*-type Si(100), and (c) HfO₂ and VO₂ on oxidized *n*-type Si(100). Dashed lines are used to represent the conduction band minimum of the oxides which is deduced from reported values of the band gap. Distances approximately represent the experimental film thickness except the depletion region in the Si which is compressed as indicated.



FIG. 7. Band alignment of (a) plasma oxidized p-type Si(100), (b) VO₂ on oxidized p-type Si(100), and (c) HfO₂ and VO₂ on oxidized p-type Si(100). Dashed lines are used to represent the conduction band minimum of the oxides which is deduced from reported values of the band gap.

is the band bending in the *n*-type substrate. Charges presumably due to defects in the oxide layers affect the band alignment which changes during growth. The VO₂/SiO₂ interface traps negative charges after the VO₂ deposition for the *n*-type sample. The fact that the VO₂ CBM is near the Fermi level enables accommodation of excess positive or negative charges. The upwards band bending of the *n*-type Si substrate indicates these positive charges accumulate at the depletion region near the interface. For both *n*- and *p*-type substrates, the band offset between the VO₂ layer and SiO₂ layer is measured as 4.0 ± 0.1 eV. According to the band alignment diagrams, both *n*- and *p*-type structures can confine the electrons and holes within the VO₂ layer. The flat band conditions of the *p*-type substrate could be more effective for confining electrons.

V. CONCLUSIONS

A gate stack structure has been prepared with HfO2 and an ultra thin VO₂ layer on oxidized Si substrates. The films were developed by reactive e-beam deposition on oxidized *n*- and *p*-type substrates. The TEM analysis confirmed the layer structure and indicated sharp interfaces without evidence of interdiffusion. The band alignment for this gate stack structure was deduced from in situ XPS and UPS spectra. A band offset of $4.0 \pm 0.1 \text{ eV}$ was measured between an ultra thin VO₂ layer and the SiO₂ layer. After the HfO₂ capping layer deposition, only small changes in the band alignment are observed. The band offset between the HfO2 and VO_2 is $3.4 \pm 0.1 \text{ eV}$. The relative band offset between the HfO₂ and SiO₂ with a VO₂ interlayer is 0.7 ± 0.1 eV which is comparable to the value without a VO₂ inter-layer. The results also show charge transfer to the VO₂ for growth on the *n*-type substrate. The band diagram for this gate stack structure shows a confined-well band structure, demonstrating the potential for charge storage for the embedded VO_2 layer.

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