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Vanadium dioxide (VO₂) is a narrow band gap material that undergoes a metal-insulator phase transition at \sim 343 K with evidence of an electric-field induced transition at T < 343 K. In this study, a sandwich-type dielectric structure is prepared consisting of two \sim 1.5 nm hafnium oxide (HfO₂) layers with a \sim 1.0 nm VO₂ interlayer grown on an oxidized n-type silicon substrate. The electronic properties of the sample were characterized by *in-situ* x-ray and ultraviolet photoelectron spectroscopy after each layer was deposited. The band alignment was analyzed after each growth step. The SiO₂/HfO₂ interface valence band offset is found to be 0.7 eV, and the HfO₂/VO₂ interface valence band offset is determined to be 3.4 eV. © 2014 American Vacuum Society. [http://dx.doi.org/10.1116/1.4832341]

I. INTRODUCTION

Vanadium dioxide (VO₂) is a narrow band gap material (Eg = 0.7 eV), with an abrupt metal to insulator transition (MIT) at \sim 70 °C (343 K).^{1,2} Results indicate that the transition temperature can be affected by strain, and results for VO_2 on TiO_2 indicate that the transition temperature can be as low as 300 K.³ Studies have also suggested that an applied electric field of $\sim 10^7$ V/m can lead to a reduction of the MIT temperature.^{4–8} The large change in electrical resistivity and optical absorption due to the MIT makes VO2 a strong candidate for a variety of optical and electronic switching applications.^{9,10} Recently, Viswanath *et al.*¹¹ have employed two HfO₂ layers to confine carriers in a VO₂ layer in a structure similar to that considered in this study. The structure displayed a reduced MIT temperature to a value as low as \sim 45 °C. To develop efficient charge storage or switching devices based on the electronic properties of VO₂, it is necessary to understand the band alignment of VO₂ relative to the dielectric interfaces and the Si substrate.

In this study, a thin VO₂ layer has been prepared as an interlayer inserted between two layers of the high-k dielectric material, HfO₂. The structures were prepared on clean, oxidized n-type Si substrates. Hafnium oxide (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.¹² In this structure, the VO₂ layer is potentially able to accept charge through tunneling from the substrate. With the high-k layers, an applied gate voltage would control the potential of the VO₂ layer relative to the substrate. The band relations for HfO₂, VO₂, and the oxidized n-type Si substrate are determined from *in-situ* photoemission measurements, and the interfacial charge transfer during the growth is discussed.

II. EXPERIMENT

The *in-situ* experiments were accomplished using an integrated ultrahigh vacuum (UHV) system constructed around a linear ~ 20 m UHV transfer line chamber (base pressure of 5×10^{-10} Torr) that connects different process and characterization chambers. In this study, the following systems were used: remote oxygen plasma for cleaning, reactive

electron beam deposition for HfO_2 and VO_2 growth, x-ray photoelectron spectroscopy (XPS) for core level analysis, and ultraviolet photoelectron spectroscopy (UPS) for valence band spectra. The sample was transferred between each chamber by a sample cart in the UHV transfer line.

The samples were grown on 25 mm dia. n-type, phosphorusdoped, (100) silicon wafers with a resistivity of 0.05–0.09 Ω ·cm. Before loading into the UHV chamber, wafers were cleaned in an ultrasonic acetone bath for 15 min, an ultrasonic methanol bath for another 15 min., and dried in ultrahigh-purity nitrogen gas. After transfer into the UHV system, the Si(100) surfaces were cleaned and oxidized by a remote oxygen plasma. The plasma exposure conditions were 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.¹³ 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. A 1.5 nm HfO₂ film was directly deposited onto the cleaned oxidized Si wafer at room temperature with an oxygen pressure of 2×10^{-6} Torr. A 1 nm thick VO₂ film was deposited onto the 1.5 nm HfO₂ layer at 550 °C with an oxygen gas pressure of 6×10^{-4} Torr. A second 1.5 nm HfO₂ film was directly deposited over the VO₂ layer with the substrate at room temperature and an oxygen pressure of 2×10^{-6} Torr. For each layer, a growth rate of 0.01 nm/s was maintained using a quartz crystal thickness rate meter.

The sample was characterized by XPS and UPS at each step. XPS characterization was 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 system was determined to be approximately 1.0 eV from the full width at half maximum of the gold $4f_{7/2}$ core level peak. However, through curve fitting, the centroid of spectral

peaks can be resolved to $\pm 0.1 \text{ eV}$. The XPS system was calibrated to align the Au $4f_{7/2}$ peak core level to 84.0 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 energy resolution of 0.15 eV. A negative bias of 4.00 eV was applied to the substrate to overcome the work function of the analyzer.

Photoemission measurements of dielectric layers can be affected by charging. In this study the conducting Si substrate in contact with the biased sample holder precludes effects of overall sample charging, and the thin dielectric layers employed here limit the effects of surface charges that would develop due to photoelectron emission. Consequently, electron compensation was not employed in these measurements. This aspect is addressed further in the appropriate sections.

III. RESULTS

The *in-situ* experiments consisted of the following processes: (1) remote oxygen plasma cleaning of the n-type Si substrate followed by a 5 min 500 °C annealing, (2) XPS and UPS characterization, (3) deposition of ~1.5 nm of hafnium oxide, (4) XPS and UPS characterization, (5) deposition of ~1.0 nm of vanadium oxide, (6) XPS and UPS characterization, (7) deposition of ~1.5 nm of hafnium oxide, and (8) XPS and UPS characterization. The XPS and UPS spectra after each step are shown in Figs. 1–4. The XPS observation "windows" were set for the Si 2p, Hf 4f, O 1s, and V 2p core levels. The carbon XPS peaks were below and close to the detection limit before and after deposition, respectively.

A. Oxidized Si substrate

The Si 2p core level for the plasma oxidized Si substrate is shown in Fig. 1. The initial SiO₂ layer thickness can be determined from the intensity ratio of the bulk (\sim 99 eV) and



FIG. 1. (Color online) X-ray photoemission spectra of the Si 2p peaks obtained after (a) plasma cleaning of the n-type Si(100) substrate, (b) deposition of the first HfO₂ layer, (c) deposition of the VO₂ interlayer on HfO₂, and (d) deposition of the second HfO₂ layer on VO₂.



Fig. 2. (Color online) X-ray photoemission spectra of the Hf 4f peaks obtained after deposition of (b) the first HfO_2 layer, (c) the VO_2 interlayer on HfO_2 , and (d) the second HfO_2 layer on VO_2 .

SiO₂ (~104 eV) Si peaks. The SiO₂ thickness was determined using the following equation:¹⁴ $t_{ox} = \lambda_{SiO_2} \ln \{[(1/\beta) (I_{SiO_2}^{exp}/I_{Si}^{exp})] + 1\}$, where λ_{SiO_2} is the attenuation length of the Si 2p photoelectrons in SiO₂, $\beta = (I_{SiO_2}^{\infty}/I_{Si}^{\infty})$ is the ratio of the Si 2p intensity from a thick SiO₂ layer and a clean Si wafer, and $I_{SiO_2}^{exp}/I_{Si}^{exp}$ 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_{SiO_2} to be 2.8 ± 0.2 nm, an average from five references,^{15–19} and β to be 0.83.¹⁹ With these values and the measured intensities ratio, the thickness of the initial SiO₂ layer on the Si wafer is determined to be 0.7 ± 0.1 nm.

The XPS binding energies of the Si 2p, O 1s, V $2p_{3/2}$, and Hf $4f_{7/2}$ core levels are summarized in Table I. The initial Si 2p peaks are at 99.7 and 103.7 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).²⁰ For the



FIG. 3. (Color online) X-ray photoemission spectra of O 1s and V 2p peaks obtained after (a) plasma cleaning of the n-type Si(100) substrate, (b) deposition of the first HfO₂ layer on Si, (c) deposition of VO₂ interlayer on HfO₂, and (d) deposition of second HfO₂ layer on VO₂.





FIG. 4. (Color online) Ultraviolet photoemission spectra obtained after (a) plasma cleaning of the n-type Si(100) substrate, (b) deposition of the first HfO_2 layer, (c) deposition of the VO_2 interlayer on HfO_2 , and (d) deposition of the second HfO_2 layer on VO_2 .

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 the first 1.5 nm HfO₂ layer deposition, the Si bulk and SiO₂ related 2p peaks shift to lower binding energies of 99.6 and 103.5 eV, respectively. After deposition of the 1.0 nm VO₂ layer, the Si bulk and SiO₂ related peaks shift to lower binding energies of 99.7 and 103.4 eV, respectively. After the second 1.5 nm HfO₂ layer deposition, the Si peaks shift back to 99.7 and 103.4 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.^{20,21}

B. HfO₂ layers

The initial 1.5 nm HfO₂ layer was deposited directly on the oxidized n-type Si substrate. The second HfO₂ layer was deposited on the VO₂ interlayer. Figure 2 presents the Hf XPS 4f peaks as evidence of the HfO₂ layers. For the first 1.5 nm HfO₂ layer on oxidized n-type Si, the Hf 4f_{7/2} peak is located at 18.3 eV. After the VO₂ interlayer deposition, the Hf 4f_{7/2} peak is located at 17.2 eV. When the second 1.5 nm HfO₂ layer was deposited on the VO₂ interlayer, the Hf 4f_{7/2} peak is located at 17.9 eV.

TABLE I. XPS of Si 2p (Si and SiO₂), O 1s, V 2p_{3/2}, Hf 4f_{7/2} core levels, and VBM relative to the Fermi level, in eV, for HfO₂/VO₂//HfO₂/oxidized *n*-type Si(100). Values have an uncertainty of ± 0.1 eV.

	Si 2p (eV)					
Process	Si bulk	SiO ₂	O 1s (eV) Main	V 2p _{3/2} (eV)	Hf 4f _{7/2} (eV)	VBM (eV)
Substrate	99.7	103.7	532.6	/	/	5.5
1.5 nm HfO_2	99.6	103.5	531.2	/	18.3	4.5
1.0 nm VO ₂	99.5	102.8	530.2	515.5	17.2	0.8
$1.5\text{nm}\text{HfO}_2$	99.7	103.4	531.0	/	17.9	4.2

The final scan after the second HfO_2 deposition displayed a weak C 1s feature. The peak was detected at ~285.1 eV, which is typical for adventitious carbon on conducting surfaces, again indicating that photoemission charging does not substantially change the potentials in this stacked structure.

C. 1.0 nm VO₂ layer

A 1.0 nm thick VO_2 interlayer was deposited between the two HfO₂ layers. The O 1s and V 2p core levels are shown in Fig. 3. The O 1s peak around $530 \sim 533 \text{ eV}$ has contributions from all of the oxide layers. However, the main peak is dominated by the top oxide layer at each growth step. For the Si substrate, the peak at 532.6 eV is the O 1s signal from oxygen in the SiO₂ layer. After the first HfO₂ layer, the O 1s peak at 531.2 eV is mostly due to oxygen in the HfO₂. After VO₂ deposition, the peak at 530.2 eV is attributed to the O 1s signal corresponding to the VO_2 layer. After the second HfO_2 capping layer, the O 1s peak at 531.0 eV is mostly due to oxygen in the second HfO₂ layer. After the initial 1.0 nm VO₂ deposition, the V $2p_{3/2}$ peak is located at 515.5 eV. After the HfO₂ deposition, the V $2p_{3/2}$ peak is broadened within a range of 513-515 eV, which may be due to the extraction of oxygen from the VO₂ layer during HfO₂ deposition. The V 2p_{3/2} peak at 513.4 eV may be due to other vanadium oxides,²² or vanadium-hafnium interface oxides. The peaks at 522 eV are the O 1s satellite peaks, which are due to the satellite lines of the nonmonochromatic Mg x-ray source.

D. Ultraviolet photoemission spectra

The UPS shown in Fig. 4 were obtained from the plasma oxidized substrate, the initial HfO_2 layer deposition, the VO_2 deposition, and the second HfO_2 layer deposition. The UPS spectrum of the initial plasma cleaned surface reflects the typical double peak structure of a SiO₂ layer on an n-type Si substrate. Extrapolation from the leading edge of the first peak indicates the VBM at 5.5 eV below the Fermi level. The valence band offset (VBO) between Si and SiO₂ is then 4.5 eV for the n-type Si substrate, which agrees with previous results.²³ This result is consistent with a low interface state density and negligible band bending for the Si substrate. In addition, the essentially flat band condition indicated by the XPS and the consistency with prior band offset measurements indicates that photoemission surface charging is not significant.

After deposition of the first 1.5 nm HfO_2 layer, the front cutoff of the UPS spectrum indicates the valence band maximum relative to the Fermi level at 4.5 eV. 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 0.8 eV below the Fermi level. After deposition of the second 1.5 nm HfO_2 layer, the front cutoff of the UPS spectrum indicates the valence band maximum relative to the Fermi level at 4.2 eV.

E. Transmission electron microscopy

Figure 5 displays a cross-sectional transmission electron micrograph of the structure. The VO₂ and HfO₂ layers are ~ 1.0 nm and 1.5 nm in thickness, respectively. The thickness of the final SiO₂ layer is ~ 1.2 nm, suggesting that the



FIG. 5. Cross-sectional high-resolution transmission electron micrograph of the HfO₂/VO₂/HfO₂/SiO₂ structure on Si.

thickness had increased due to substrate oxidation during the higher temperature growth of the VO_2 layer. This is also consistent with the XPS results. From Fig. 1, the ratio of

XPS intensities $(I_{SiO_2}^{exp}/I_{Si}^{exp})$ is found to be 0.25 for the initial oxidized Si substrate which increases to 0.79 for the final sample. Using the analysis described in Sec. III A, the XPS result indicates that the SiO₂ layer has grown to 1.9 nm after deposition of the oxide layers. This is greater than indicated by the TEM results and may represent systematic differences or the limit of approximations used in the XPS analysis. 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/HfO₂, and HfO₂/VO₂/HfO₂ interfaces. The results indicate an amorphous structure and sharp interfaces without evidence of intermixing.

IV. DISCUSSION

Figure 6 shows the deduced diagrams of the band alignment for the stacked structure during processing. It is noted that the conduction band minimum for all of the oxides



FIG. 6. Band schematics (a) of the oxidized Si substrate, (b) after deposition of the first HfO₂ layer, (c) after deposition of the VO₂ interlayer, and (d) after deposition of the second HfO₂ layer. Dashed lines represent the conduction band minimum of the oxides, which are deduced from reported band gap values. Distances approximately represent the experimental film thickness with the exception of the depletion region in the Si (\sim 17 and \sim 24 nm for 0.1 and 0.2 eV upward band bending, respectively), which is compressed as indicated.

(shown as dashed lines in the figures) are deduced from the reported values of the band gap. The initial cleaned oxidized Si substrate displays a flat band condition, shown in Fig. 6(a), and as noted previously, the result is consistent with prior reports.

After the initial 1.5 nm HfO₂ deposition, the band schematic is represented in Fig. 6(b). The HfO₂ VBM is at 4.5 eV below E_f from UPS measurement. The SiO₂ bands are tilted upwards toward the surface, indicating the presence of negative charge near the HfO₂–SiO₂ interface, which is consistent with prior results.²⁴ A recent study has indicated that surface states can also contribute to an electric field across the dielectric layer.²⁵ With the much larger dielectric constant of the HfO₂ versus SiO₂, it is presumed that any electric potential change across the high-k HfO₂ layer can be neglected.²⁰

Consequently, the potential at different depths in the SiO_2 layer will be different, and the valence band offset between HfO_2 and SiO_2 can be determined using the following expression:

$$\begin{split} \text{VBO} &= (\text{E}_{4\text{f}7/2}{}^{\text{HfO}_2} - \text{E}_{\text{VBM}}{}^{\text{HfO}_2}) - (\text{E}_{2\text{p}}{}^{\text{SiO}_2} - \text{E}_{\text{VBM}}{}^{\text{SiO}_2}) \\ &- \Delta 1(\text{E}_{4\text{f}7/2}{}^{\text{HfO}_2} - \text{E}_{2\text{p}}{}^{\text{SiO}_2}) - \Delta 2(\text{SiO}_2), \end{split} \tag{1}$$

where $(E_{4f7/2}{}^{HfO_2} - E_{VBM}{}^{HfO_2})$ is the Hf $4f_{7/2}$ core level to the VBM of HfO_2; $(E_{2p}{}^{SiO_2} - E_{vbm}{}^{SiO_2})$ is the Si 2p core level to the VBM of SiO_2; $\Delta 1(E_{4f7/2}{}^{HfO_2} - E_{2p}{}^{SiO_2})$ is the energy separation between the Hf $4f_{7/2}$ of HfO_2 and Si 2p of SiO_2; and $\Delta 2(SiO_2)$ is approximately the half value of the electrical potential across the SiO_ layer.

According to the analysis by Fulton *et al.*,²⁶ the centroid position of the core level spectra for a 1.2 nm SiO₂ layer would be at 0.56 nm from the outer surface, which in this case is approximated as the center of the film. Therefore, the XPS is assumed to measure the center position of the SiO₂ layer. For thicker layers, the $\Delta 2(SiO_2)$ term of Eq. (1) would reflect the potential difference from the layer surface to the centroid position. We note that the width of the SiO₂-related Si 2p peak precludes more detailed analysis. Based on the 0.2 eV shift of the SiO₂-related Si 2p peak and the ~0.1 eV shift of the substrate Si 2p peak (indicting band bending), the electrical potential across the SiO₂ layer is calculated as 0.2 eV [i.e., $2 \times (0.2 - 0.1) \text{ eV}$]. The XPS core level values and the energy differences for the VBO calculations are summarized in Tables I and II, respectively. The VBO of HfO_2 and SiO_2 is then calculated as 0.7 eV.

We note that this analysis assumes the HfO_2 and SiO_2 layers do not interdiffuse at the low deposition and processing temperatures used in this study. Intermixing could be reflected in the relative separation of the Si 2p in Si and SiO_2 and the energy difference of Hf $4f_{7/2}$ to VBM. The energy difference of the Si 2p in Si and SiO₂ after plasma cleaning, first layer HfO₂ deposition, VO₂ deposition, and second layer HfO₂ deposition were 4.0, 3.9, 3.3, and 3.7 eV, respectively. The energy difference after the final room temperature HfO₂ deposition was close to the value before VO₂ deposition, indicating that interdiffusion was not the likely cause of the shift, and that the variations instead reflected the internal electric field in the SiO₂ layer. The energy difference of the Hf $4f_{7/2}$ to VBM in the first and second HfO₂ layers are 13.8 and 13.7 eV, respectively, which is consistent with previous reports from our group $(13.6-13.9 \text{ eV})^{27,28}$ and other reports (13.8 eV).²⁹ Both results indicate that formation of intermixed HfSiO_x is not significant at the low deposition and annealing temperatures of this study.

However, during the higher temperature growth of VO₂, the oxygen may diffuse through HfO_2 layer and enhance the thickness of the SiO₂ layer, which was evidenced by the increased Si 2p (SiO₂) intensity relative to the substrate Si 2p signal.

After the VO₂ layer deposition, the Si 2p and Hf $4f_{7/2}$ peaks shift to lower binding energy, indicating an electric potential across the SiO₂ layer and band bending in the Si substrate, shown in Fig. 6(c). After the second HfO₂ layer deposition, the Si 2p and Hf 4f7/2 peak shifts approach the band condition of the initial HfO_2 layer, shown in Fig. 6(d). The 3.4 eV HfO₂/VO₂ valence band offset is consistent with a previous study from our group.²⁸ However, in Fig. 6(c), the VO₂/HfO₂ band offset is indicated as 2.6 eV. This difference may be due to the processing sequence. We suggest that the VO₂/HfO₂ interface after the higher temperature growth of the VO₂ layer on the first HfO₂ layer may be different from the HfO_2/VO_2 interface after the room temperature growth of the second HfO₂ layer. During higher temperature VO₂ deposition, some of the oxygen in the first HfO₂ layer may diffuse into the VO₂ film. When the second HfO_2 layer is deposited on the VO₂ layer at room temperature, oxygen may diffuse into the structure and compensate the oxygen deficiency of the first HfO₂ layer.

For most heterostructures, interface bonding leads to charge transfer and an interface dipole. The interfacial dipole is often described as the difference between the vacuum levels at the interface of the two adjoining materials. Experimentally, this can be determined from the UPS results using:

$$\Delta \text{Dipole} = (h\nu - W^{a}) - (h\nu - W^{b}) - VBO^{a/b}$$
$$= W^{b} - W^{a} - VBO^{a/b}, \qquad (2)$$

where W^a and W^b represent the width of the UPS spectra from the VBM to the low energy cutoff for each material.

TABLE II. Binding energy difference of $(E_{4f7/2}^{HfO_2} - E_{VBM}^{HfO_2})$, $(E_{2p}^{SiO_2} - E_{VBM}^{SiO_2})$, $\Delta 1(E_{4f7/2}^{HfO_2} - E_{2p}^{SiO_2})$, $\Delta 2(SiO_2)$, $(E_{2p3/2}^{VO_2} - E_{VBM}^{VO_2})$, and $\Delta 3(E_{2p3/2}^{VO_2} - E_{4f7/2}^{HfO_2})$. All energies are given in eV.

Process	$(E_{4f7/2}{}^{HfO_2} - E_{VBM}{}^{HfO_2})$	$(E_{2p}^{SiO_2} – E_{VBM}^{SiO_2})$	$\Delta 1(E_{4f7/2}{}^{HfO_2}-\!E_{2p}{}^{SiO_2})$	$\Delta 2(SiO_2)$	$(E_{2p3/2}{}^{VO_2} - E_{VBM}{}^{VO_2})$	$\Delta 3(E_{2p3/2}{}^{VO_2}-E_{4f7/2}{}^{HfO_2})$
1.5 nm HfO ₂	13.8	98.2	-85.2	0.1	-	_
1.0 nm VO ₂	13.8	98.2	-85.6	0.7	514.7	498.3
$1.5nm\;HfO_2$	13.7	98.2	-85.5	0.3	-	-

The deduced vacuum levels for each material are indicated in the schematics shown in Fig. 6.

For semiconductor interfaces, the charge neutrality level (CNL) model has been proposed by Tejedor and Floress,³⁰ and CNLs have been calculated by Tersoff³¹ by considering the available states at the semiconductor interface. Semiconductor bands are aligned at CNLs, which reflect the point where the contribution from donor- and acceptor-like interface induced gap sates are equal.³² This model was further modified to consider Fermi level pinning at the interface by applying a pinning factor, S, and the model was extended to dielectric interfaces.³³ According to this model the VBO of HfO₂ with respect to SiO₂ is given by the following equation:

$$\Delta E_{V} = E_{CNL,HfO_{2}} - E_{CNL,SiO_{2}} - S[I_{SiO_{2}} - I_{HfO_{2}} - (E_{CNL,SiO_{2}} - E_{CNL,HfO_{2}})], \quad (3)$$

where E_{CNL,HfO_2} and E_{CNL,SiO_2} are the charge neutrality levels of HfO₂ [3.7 eV (Ref. 33)] and SiO₂ [4.5 eV (Ref. 34)] with respect to VBM; S is the pinning factor of the larger band gap material, SiO₂ [0.86 (Ref. 34)]; I_{SiO_2} and I_{HfO_2} are the photothreshold energies of SiO₂ (9.7 eV) and HfO₂ (8.5 eV), which is equal to the sum of band gap and electron affinity. In this study, the photothreshold was experimentally obtained from the difference of the width of the respective UPS spectrum and UV photon energy. Using Eq. (3), the VBO of HfO₂ and SiO₂ is expected to be -1.1 eV. On the other hand, the empirically calculated CNLs of SiO₂ and HfO₂ are 3.5 and 2.3 eV, respectively,³² which indicate a -1.2 eV value for the VBO. Both analysis are somewhat larger than the -0.7 eV value deduced in this research.

V. CONCLUSIONS

A confined well structure has been prepared with an ultrathin VO₂ layer between two HfO₂ layers. The films were prepared by reactive e-beam deposition on oxidized n-type Si substrates. The band alignment for this gate stack structure was deduced from *in-situ* XPS and UPS spectra. A band offset of 0.7 ± 0.1 eV was measured between the 1.5 nm HfO₂ layer and the SiO₂ layer, which is smaller than the value predicted by the CNL models. After deposition of the VO₂ interlayer and the HfO₂ capping layer deposition, the band offset between the HfO₂ and VO₂ is 3.4 ± 0.1 eV. The band diagram for this structure shows a confined-well band structure, demonstrating the potential for charge storage in the embedded VO₂ layer.

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