On the Dependence of Band Alignment of SiO$_2$/Si Stack on SiO$_2$ Thickness: Extrinsic Or Intrinsic?

YONGGUI XU$^1$, KAI HAN$^1$, JINJUAN XIANG$^2$, AND XIAOLEI WANG$^2$, (Member, IEEE)

$^1$Department of Physics and Optoelectronic Engineering, Weifang University, Weifang 261061, China
$^2$Key Laboratory of Microelectronics Devices and Integrated Technology, Institute of Microelectronics of Chinese Academy of Sciences, Beijing 100029, China

Corresponding authors: Kai Han (hankai@wfu.edu.cn) and Jinjuan Xiang (xiangjinjuan@ime.ac.cn)

This work was supported by the National Natural Science Foundation of China under Grant 61674003 and Grant 61404093.

ABSTRACT The dependence of band alignment of SiO$_2$/Si stack on SiO$_2$ thickness is restudied. The band structure of SiO$_2$/Si stack is investigated by time-dependent X-ray photoelectron spectroscopy (XPS) with and without electron-compensation technology. The binding energy difference $\Delta$Si$_2p$ between Si 2p core-levels of SiO$_2$ and Si, measured without electron-compensation, is found larger than that with electron-compensation, owning to the charging effect. And more severe charging effect induces larger $\Delta$Si$_2p$. The $\Delta$Si$_2p$ measured with electron-compensation technology, however, is scarcely affected by the charging effect and thus accurate band alignment can be obtained. The band alignment of SiO$_2$/Si stack is found to be SiO$_2$ thickness dependent. And this dependence is attributed to the gap states on the SiO$_2$ surface and their lower charge neutrality level than the Fermi level of Si substrate, resulting in electron transfer from Si to SiO$_2$ and electric potential distribution across the SiO$_2$. As a result, the experimentally obtained dependence of $\Delta$Si$_2p$ on SiO$_2$ thickness with electron-compensation is intrinsic. The proposed explanation about the XPS results further confirms the feasibility of the gap state theory in demonstrating the band lineup of hetero-structures.

INDEX TERMS Band alignment, hetero-structure, SiO$_2$/Si stack, XPS.

I. INTRODUCTION

Complete understanding of electronic structure and band alignment of SiO$_2$/Si stack is rather essential because this structure is fundamental and ubiquitous in Si based metal-oxide-semiconductor field effect transistor (MOSFET) [1], [2]. Even though this stack seems so familiar and is widely investigated since its introduction in the 1970s, the dependence of band alignment of this structure on SiO$_2$ thickness, or namely the binding energy difference $\Delta$Si$_2p$ between Si 2p core-levels of SiO$_2$ and Si substrate, is still perplexing [3]–[12]. Four possible explanations were proposed to elucidate this thickness dependence of band structure: (1) initial state effects such as Si–O ring size, strain, stoichiometry and crystallinity [5], [7], [10], (2) final state effects such as changes in the extra atomic relaxation energy and screening mechanism [3], [6]–[8], [10], (3) extrinsic charging effect during the X-ray photoelectron spectroscopy (XPS) measurements [4], [7], [9], [10], and (4) gap states on the SiO$_2$ surface proposed by our group [12].

The initial state effects were found not contribute to this phenomenon both experimentally and theoretically and thus ruled out [7], [8], [11]. Zhang et al. [7] constructed a structurally homogeneous silicon oxide on Si substrate with all Si atoms in identical bonding configurations and exhibiting spherical symmetry by using H$_8$Si$_8$O$_{12}$ cluster, i.e., all Si atoms in SiO$_2$ were with same Si–O ring size, strain, stoichiometry and crystallinity regardless of the SiO$_2$ thickness. And they found that the band alignment of SiO$_2$/Si structure was still SiO$_2$ thickness dependent. Thus the initial state effects were experimentally ruled out. Pasquarello [8] proceeded a first principles investigation of Si 2p core-level shifts at SiO$_2$/Si interface using pseudopotential approach, and found that structural deformations such as those implied by the distribution of Si–O bond lengths in amorphous SiO$_2$ yielded distributions of core-level shifts that were too small to account for the observed dependence of band alignment of SiO$_2$/Si structure on the SiO$_2$ thickness. Consequently, the initial state effects were also theoretically excluded.

The associate editor coordinating the review of this manuscript and approving it for publication was Ravibabu Mulaveesala.
The final state effect can also be ruled out. The final state effect was reported to play an important role for SiO₂/Si interfaces for SiO₂ films less than 3 nm [7]. In our previous experiments [12], however, thick SiO₂ of more than 4.5 nm were employed to discuss the evolution of band alignment as a function of SiO₂ thickness. And the band alignment of SiO₂/Si stack was still found to be SiO₂ thickness dependent. Thus considering that the final state effects is negligible for the SiO₂ film of more than 3 nm, the final state effect can also be excluded by our previous experimental phenomenon.

The third possible origin, i.e., the charging effect during the XPS measurements, needs further investigation. In the past the dependence of band alignment of SiO₂/Si structure on the SiO₂ thickness was investigated by XPS without electron-compensation technique. Under such condition the charging effect occurs due to the insulator characteristic of the SiO₂ film. Then positive charges accumulate in the SiO₂ films, with most of the induced charges near the surface region of SiO₂ film. These positive charges induce downward energy band bending on the surface of SiO₂, as shown in the Figure 1. Larger downward band bending is induced with thicker SiO₂, and thus the binding energy difference \( \Delta Si_{2p} \) between Si 2p core-levels of SiO₂ and Si substrate increases with thicker SiO₂. After decades of development of XPS equipment, however, the electron-compensation technique is widely used in the XPS tools such as Thermo Scientific ESCALAB 250Xi, PHI 5000 Versa Probe-II and so on. And the charging effect is considered to be minimized by nearly neutralizing the insulator film based on employing this technique. Thus the charging effect occurs without the electron-compensation technique while it does not occur with electron-compensation. Then we can evaluate the influence of charging effect on the binding energy difference \( \Delta Si_{2p} \) by using electron-compensation or not. To our knowledge there is no reported investigation on the influence of electron-compensation on the binding energy difference \( \Delta Si_{2p} \) as a function of SiO₂ thickness. Then it is necessary to directly compare the XPS results obtained with and without electron-compensation technique. In addition, it is well known that the neutralization technique used in XPS cannot exactly neutralize the X-ray exposed film but makes the film contain excess electrons on the film surface, i.e., the film is under over-electron-compensation state. In other word, the film under this condition contains excess negative charges, resulting in negative shift of the core-level binding energy compared to the true value. This over-electron-compensation can be regarded as also charging effect or more accurately negative charging effect to distinguish the above positive charging effect. Thus it is also essential to assess the influence of this over-electron-compensation on the binding energy difference \( \Delta Si_{2p} \) as a function of SiO₂ thickness.

In this paper, the influence of the charging effect on the band structures of SiO₂/Si stack with various SiO₂ thicknesses is firstly evaluated by XPS with and without electron-compensation. It is found that larger binding energy difference \( \Delta Si_{2p} \) is induced when there is no electron-compensation compared to the value with electron-compensation, i.e., charging effect induces larger \( \Delta Si_{2p} \). Then the influence of charging effect is quantitatively evaluated. And it is found that the binding energy difference \( \Delta Si_{2p} \) is scarcely affected by negative charging effect when electron-compensation technique is used even though positive charging effect shows a significant effect when electron-compensation technique is not used. Thus we can obtain the conclusion that the dependence of band alignment of SiO₂/Si stack on the SiO₂ thickness is not due to the charging effect. Then the concepts of gap states and charge neutrality level are employed to explain this SiO₂ thickness dependent shift. The gap states on the SiO₂ surface are considered to contribute to this phenomenon. So the dependence of band alignment of SiO₂/Si stack on the SiO₂ thickness is not extrinsic (charging effect) but intrinsic (gap states on the SiO₂ surface). Furthermore the work in this paper further confirm the feasibility of the theory based on gap states and charge neutrality level in explaining the band alignment of hetero-structures.

II. EXPERIMENTAL DETAILS

A. FABRICATION OF SAMPLES FOR XPS MEASUREMENTS

The experimental samples used here are same to those in our previous work [12]. After the RCA (Radio Corporation of America) clean and diluted HF immersion, high quality SiO₂/Si stack was thermally grown on 8-inch n-Si substrate using AMAT Centura HT equipment. Three SiO₂ thicknesses of 4.5 nm, 6.0 nm and 8.0 nm, which were calibrated by spectroscopic ellipsometry and X-ray reflectometry, were prepared for XPS measurements.

B. DETAILS FOR XPS MEASUREMENTS

The XPS were recorded using Thermo Scientific ESCALAB 250Xi equipped with a monochromatic Al K radiation source.
of 1486.8 eV. Binding energy calibration was performed using Au, Ag, and Cu standard samples by setting the Au 4f7/2, Ag 3d5/2, and Cu 2p3/2 peaks at binding energies of 83.98±0.02 eV, 368.26±0.02 eV, and 932.67±0.02 eV, respectively. The power of the X-ray was 216.86 W, with voltage and current of the X-ray source being 14554.20 V and 0.0149 A, respectively. All the high resolution spectra were collected at a photoelectron take off angle of 90° relative to the sample surface, and with pass energy of 20 eV. Two modes were employed for the XPS measurements. The first mode was that the electron-compensation was closed during the measurements, and the other mode was with the electron-compensation. During the measurements without electron-compensation, the Si 2p core-level binding energy was recorded as a function of X-ray irradiation time ranging from 0 to 200 min. The Si 2p spectra were fitted by a nonlinear Gaussian-Lorentzian line shape and Shirley background with a fixed spin orbit splitting of 0.61 eV and branch ratio of 1/2 for Si 2p1/2 to Si 2p3/2.

C. FABRICATION OF METAL-OXIDE-SEMICONDUCTOR (MOS) CAPACITORS FOR CAPACITANCE-VOLTAGE (C-V) MEASUREMENTS

The details of Si surface clean and thermal growth of SiO2 are same as the samples for XPS measurements. After the RCA clean and diluted HF immersion, high quality SiO2/Si stack were thermally grown on 8-inch n-Si substrate using AMAT Centura HT equipment, with SiO2 stack were thermally grown on 8-inch n-Si substrate using EPMA 1500. The details of Si surface clean and thermal growth of SiO2 are same as the samples for XPS measurements. After the removal of backside native SiO2, 700 nm Al was deposited on the backside of Si substrate using PVD. Finally all samples were annealed at 400 °C in N2 + 5% H2 ambient for backside ohmic contact formation.

D. DETAILS FOR C-V MEASUREMENTS

The C-V measurements were performed at 1 MHz by Keithley 4200. The equivalent oxide thickness (EOT) and flatband voltage (VFB) are extracted from the C-V fitting with quantum effect correction.

III. RESULTS AND DISCUSSION

A. SPECTRA OF Si 2P OF SiO2/Si STACK WITH ELECTRON-COMPENSATION

Figure 2 shows XPS spectra of Si 2p core-level of the three samples where electron-compensation technique is employed. The spectrum for each period of narrow scan of Si 2p core-level region during the XPS measurement is rather identical for both the position and shape. The Si 2p spectrum of every sample can be well fitted by two chemical states. The spectroscopic peak located at low binding energy side is attributed to photoemission from Si substrate, and the peak at higher binding energy is originated from SiO2. The sub-oxidation states of Si 2p core-level are not analyzed here because the emission intensity from sub-oxide is small enough to ignore as shown in Figure 2. The detailed analysis for inconsideration of Si sub-oxidation has been given in our previous work [12].

The position of Si 2p core-level spectrum shown in Figure 2 is in agreement with the widely reported value for true position of Si 2p core-level, which is approximately in the range of 98-101 eV for Si 2p from Si substrate and 102-106 eV for Si 2p from SiO2 [13]–[18]. The peak binding energies of Si 2p3/2 core-level obtained by fitting the spectra in Figure 2 are summarized in Table 1.

| Thickness of SiO2 (nm) | Binding energy of core-level (eV) |
|------------------------|----------------------------------|
|                        | Si 2p2 for Si substrate | Si 2p2 for SiO2 | C 1s |
| 4.5                    | 99.38                    | 103.58          | 284.98 |
| 6.0                    | 99.50                    | 103.64          | 284.92 |
| 8.0                    | 99.72                    | 103.86          | 285.11 |

The XPS spectra of C 1s core-level for the three samples to evaluate the charging level. Figure 3 shows the XPS spectra of C 1s for the three samples. It can be seen that all spectra can be fitted by two chemical states, with the peak located at low binding energy originating from C-H bond and that at high binding energy from C-O bond. The binding energy of C 1s core-level of C-H bond is summarized in Table I. It can be seen that the peak binding energy of C 1s core-level for C-H bond is not just right localized at 284.8 eV, which is considered as the true value for C 1s core-level of C-H bond. This indicates that the measured samples are not just right neutralized by using electron-compensation technique. The binding energies of C 1s core-level localize at 284.98 eV, 284.92 eV and 285.11 eV for 4.5-nm-SiO2/Si, 6.0-nm-SiO2/Si and 8.0-nm-SiO2/Si, respectively. They are all larger than 284.8 eV, indicating that the X-ray irradiated
of charging effect using Si 2p core-level is not more than 0.15 eV considering the uncertainty of the true value for Si 2p core-level, which is the central topic of this paper. Each spectrum in Figure 5 can be well fitted by two chemical states. The peak located at low binding energy is due to photoemission from Si substrate with that at high binding energy from SiO2. The suboxidation states of Si 2p core-level are not analyzed because the emission intensity from suboxide is small enough to ignore as shown in Figure 5.

Figure 6 shows the Si 2p core-level binding energy and the ΔSi_2p as a function of X-ray irradiation time. The peak position is determined by fitting the spectrum. The Si 2p peaks of 4.5-nm-SiO2/Si stack as shown in Figure 6(a) increase firstly and then decrease. This phenomenon is consistent with the reported results [19]–[23]. A shift toward higher binding energy indicates that the amount of positive charges in the oxide is increasing, and the following shift toward a lower binding energy indicates that the amount of negative charges is increasing. These correspond to the hole-trapping and subsequent electron-trapping in the SiO2 [20]–[22]. The shape of Si 2p spectrum, however, is nearly identical as a function of X-ray irradiation time. The ΔSi_2p is nearly unchanged and 4.34 eV for 4.5-nm-SiO2/Si stack, which is 0.15 eV larger than that of 4.19 eV when electron-compensation technique is used as shown in Figure 4. It should be stated again that in the XPS measurements with electron-compensation, no shift of Si 2p core-level spectrum was found as a function of X-ray irradiation time, and each spectrum was identical for measuring Si 2p core-level of SiO2/Si stack as a function of SiO2 thickness.

FIGURE 3. XPS spectra of C 1s core-level for 4.5-nm-SiO2/Si stack, 6.0-nm-SiO2/Si stack, and 8.0-nm-SiO2/Si stack. Similar to the case in Fig. 2, there is electron-compensation during the XPS measurements.

FIGURE 4. The ΔSi_2p of SiO2/Si stack as a function of SiO2 thickness when the electron-compensation technique is used during the XPS measurements.

parameters to confirm this variation trend. Then the question is to quantitatively estimate the effect of this positive charging effect on the ΔSi_2p. This will be described in the following sessions. In the next session, we measure the ΔSi_2p when electron-compensation technique is not used, and significant charging effect can be observed. Thus we can obtain the experimental data about the influence of charging effect on the ΔSi_2p. Then a model is established to quantitatively assess the influence of charging effect on the ΔSi_2p.

B. SPECTRA OF SI 2P OF SiO2/Si STACK WITHOUT ELECTRON-COMPENSATION

Figure 5 shows the Si 2p core-level spectra as a function of X-ray irradiation time under the mode without electron-compensation technique. Owning to the positive charging effect, the Si 2p core-level spectra of 4.5-nm-SiO2/Si stack in Figure 5(a) are located in the range of 130-140 eV, 30-40 eV larger than the real Si 2p binding energy of ~100 eV. The Si 2p core-level spectra of 6.0-nm-SiO2/Si stack in Figure 5(b) are located in the range of 455-465 eV, 355-365 eV larger than the real Si 2p binding energy of ~100 eV. The Si 2p core-level spectra of 8.0-nm-SiO2/Si stack in Figure 5(c) are located in the range of 110-120 eV, 10-20 eV larger than the real Si 2p binding energy of ~100 eV. It should be noted that the charging degree does not increase with thicker SiO2 and increases in the following sequence: 8-nm-SiO2/Si, 4.5-nm-SiO2/Si and 6.0-nm-SiO2/Si. The reason is unclear and needs further investigation. These, however, do not affect the quantitative evaluation of influence of charging effect on the binding energy difference ΔSi_2p, which is the central topic of this paper. Each spectrum in Figure 5 can be well fitted by two chemical states. The peak located at low binding energy is due to photoemission from Si substrate with that at high binding energy from SiO2. The suboxidation states of Si 2p core-level are not analyzed because the emission intensity from suboxide is small enough to ignore as shown in Figure 5.

Figure 6 shows the Si 2p core-level binding energy and the ΔSi_2p as a function of X-ray irradiation time. The peak position is determined by fitting the spectrum. The Si 2p peaks of 4.5-nm-SiO2/Si stack as shown in Figure 6(a) increase firstly and then decrease. This phenomenon is consistent with the reported results [19]–[23]. A shift toward higher binding energy indicates that the amount of positive charges in the oxide is increasing, and the following shift toward a lower binding energy indicates that the amount of negative charges is increasing. These correspond to the hole-trapping and subsequent electron-trapping in the SiO2 [20]–[22]. The shape of Si 2p spectrum, however, is nearly identical as a function of X-ray irradiation time. The ΔSi_2p is nearly unchanged and 4.34 eV for 4.5-nm-SiO2/Si stack, which is 0.15 eV larger than that of 4.19 eV when electron-compensation technique is used as shown in Figure 4. It should be stated again that in the XPS measurements with electron-compensation, no shift of Si 2p core-level spectrum was found as a function of X-ray irradiation time, and each spectrum was identical for measuring Si 2p core-level of SiO2/Si stack as a function of SiO2 thickness.

samples with electron-compensation are positively charged even though the electron-compensation technique is used during the measurements. The extent of this positive charging effect can be approximately evaluated by the measured peak position compared with the true value (284.8 eV), which is about 0.3 eV by using C 1s core-level. Similarly the extent of charging effect using Si 2p core-level is not more than 1 eV considering the uncertainty of the true value for Si 2p core-level.

Figure 4 shows the binding energy difference ΔSi_2p between Si 2p core-levels of SiO2 and Si substrate as a function of SiO2 thickness. It can be seen that the ΔSi_2p decreases when the thickness of SiO2 increases from 4.5 nm to 6.0 nm, and then saturates from 6.0 nm to 8.0 nm. In our previous work [12], we have also utilized the Auger
both peak position and shape. Figure 6(b) shows the Si 2p core-level binding energy and the $\Delta Si \ 2p$ as a function of X-ray irradiation time for 6.0-nm-SiO$_2$/Si stack. The signal in the first 115 min is not shown here because of the very sharp increase of the Si 2p core-level binding energy, which is difficult to acquire during narrow scan of high energy resolution. However, it is reasonable to conclude that the Si 2p spectrum of 6.0 nm SiO$_2$/Si stack increases firstly and then decreases. The shape of Si 2p spectrum is unchanged as a function of X-ray irradiation time. Finally the $\Delta Si \ 2p$ stabilizes at 4.52 eV, which is 0.38 eV larger than that of 4.14 eV with electron-compensation as shown in Figure 4. The Si 2p binding energy of 8.0-nm-SiO$_2$/Si stack in Figure 6(c) shows a slightly different variation trend. The binding energy of Si 2p core-level increases initially and then saturates, with the $\Delta Si \ 2p$ stabilizing at 4.20 eV, which is 0.06 eV larger than that of 4.14 eV with electron-compensation in Figure 4. The somewhat different variation trend of Si 2p core-level binding energy of 8.0-nm-SiO$_2$/Si stack in Fig. 6(c) compared with that for 4.5- or 6.0-nm-SiO$_2$/Si in Figure 6(a) or 6(b) may be related with some SiO$_2$ thickness dependent characteristic, which needs further investigation. Fortunately these do not affect the evaluation of the charging effect.
expressed as follows[18]:

\[ \Delta \delta_{Si\_2p} = 2e_0 \frac{d_{oxide}}{e_0} \delta_{Si\_2p} \]  

(2)

The variation of binding energy difference between core-levels of SiO\textsubscript{2} and Si substrates \( \Delta \delta_{Si\_2p} \), induced by this effective charge density per unit of area, is approximately given by

\[ \Delta \delta_{Si\_2p} = -\frac{eN}{2e_0} d_{oxide} \delta_{Si\_2p} \]  

(3)

where the \( d_{oxide} \) expresses the SiO\textsubscript{2} oxide thickness. Then based on equation (3) it can be obtained that for SiO\textsubscript{2} thickness of 6 nm, the \( \delta_{Si\_2p} \) of 10 eV corresponds to the \( \Delta \delta_{Si\_2p} \) of 1 meV, which is approximately consistent with the experimental results of 7.6-56 meV for \( \Delta \delta_{Si\_2p} \) per 10 eV for \( \delta_{Si\_2p} \). The deviation maybe come from the exact value of \( d_0 \). All of these show that the \( \delta_{Si\_2p} \) of less than 10 eV has a nearly negligible effect on the accurate value of \( \Delta \delta_{Si\_2p} \). In other words, i.e., even though the absolute value of binding energy is relatively largely affected by the charging effect, the binding energy difference between two core-levels is scarcely affected and consequently survived. Especially the binding energy of Si 2p core-level was located in the range of \( \sim 99-103 \) eV when the electron-compensation technique was employed, indicating that the influence of charging effect on \( \Delta \delta_{Si\_2p} \) is so weak that it can be ignored reasonably. Thus the binding energy difference between core-levels are accurately obtained within any charging effect when the electron-compensation technique is employed during the XPS measurements.

D. THE EXCLUSION OF THE CHARGING EFFECT ACCOUNTING FOR THE SiO\textsubscript{2} THICKNESS DEPENDENCE OF BAND ALIGNMENT OF SiO\textsubscript{2}/Si STACK

As shown in the previous section, the binding energy difference \( \Delta \delta_{Si\_2p} \) between core-levels can be precisely determined when the electron-compensation technique is employed, i.e., the nearly negligible charging effect with electron-compensation technology does not affect the \( \Delta \delta_{Si\_2p} \) value. Based on the experimental results in Sec. 3.1, the band alignment of SiO\textsubscript{2}/Si stack still shows SiO\textsubscript{2} thickness dependence when the electron-compensation technology is employed. Thus we can exclude the charging effect as the physical origin of this SiO\textsubscript{2} thickness dependence of band alignment of SiO\textsubscript{2}/Si stack in our experiments.

E. THE EXCLUSION OF INTERFACIAL OR BULK CHARGE DISTRIBUTION ACROSS THE SiO\textsubscript{2}/Si STACK ACCOUNTING FOR THE SiO\textsubscript{2} THICKNESS DEPENDENCE OF BAND ALIGNMENT OF SiO\textsubscript{2}/Si STACK

This section discusses the possible effect of charge distribution on the band alignment of SiO\textsubscript{2}/Si stack. The charge distribution here means the interfacial (at SiO\textsubscript{2}/Si interface) and/or bulk (in SiO\textsubscript{2}) charges located in the gate.
and the charges induced by the X-ray irradiation during the XPS measurements. These charges are widely reported for MOS gate structure with high-k materials and metal gate [24]–[26]. As previously reported [13], [15], [27], the charge distribution can induce the electric potential variation across the gate stack, which changes the value of core-level binding energy. Thus the effect of charge distribution on the band alignment of SiO$_2$/Si stack needs investigation.

Figure 8 shows the C-V curves of TiN/SiO$_2$/Si MOS capacitor for different SiO$_2$ thicknesses. It can be seen that well C-V shape is obtained. Figure 9 shows the flatband voltage ($V_{FB}$) as a function of SiO$_2$ thickness ($T_{SiO2}$) by fitting the C-V curves in Fig. 8 considering the quantum effect. Then the densities of interfacial charges at SiO$_2$/Si interface and bulk charges in SiO$_2$ can be obtained to be $+7.55 \times 10^{10}$ #/cm$^2$ and 0 #/cm$^3$, respectively, by the following formula:

$$V_{FB} = \phi_{ms} - \frac{Q_{SiO2, Si}}{\varepsilon_0 \varepsilon_{SiO2}} T_{SiO2} - \frac{\rho_{bulk, SiO2}}{2 \varepsilon_0 \varepsilon_{SiO2}} T_{SiO2}^2$$

(4)

where the $\phi_{ms}$ is the vacuum workfunction difference between TiN and Si substrate, $Q_{SiO2, Si}$ is the areal charge densities (per unit area) at the SiO$_2$/Si interface, $\rho_{bulk, SiO2}$ is the bulk charge densities (per unit volume) in SiO$_2$, $\varepsilon_0$ and $\varepsilon_{SiO2}$ express the vacuum permittivity and the relative permittivity of SiO$_2$, respectively. Then based on Equation (4), it can be seen that the $V_{FB}$ is a quadratic function of $T_{SiO2}$, with the linear and quadratic terms determining the values of charges at SiO$_2$/Si interface and in SiO$_2$. Also shown in the Fig. 9 is the fitting formula of experimental $V_{FB}$-$T_{SiO2}$ data. By comparing this formula with equation (4) we can obtain the charge distribution across the SiO$_2$/Si stack, i.e., interfacial charges at SiO$_2$/Si interface and in SiO$_2$. These results in our experiment are in good agreement with the reported values in the literature [25], [28], [29]. The reason why the quadratic term in Eq. 4 is not evident in Fig. 9 is that the bulk charges in the thermal SiO$_2$ are rather small and cannot be detected by the experiment. This means that the thermal oxidation of Si at $\sim 1050$ ºC in our experiments results in high quality SiO$_2$. The traps in the SiO$_2$ are rather small and can be ignored.

The charge distribution has no effect on the band alignment of SiO$_2$/Si stack as a function of SiO$_2$ thickness. Firstly the effect of bulk charges in SiO$_2$ is discussed. From the above experimental results it can be seen that the bulk charges in SiO$_2$ is 0 #/cm$^3$. Thus these charges do not induce electric potential across the SiO$_2$/Si stack, i.e., no effect on the band alignment of SiO$_2$/Si stack. Then the effect of interfacial charges at SiO$_2$/Si interface is evaluated. These positive charges induce upward band bending toward the SiO$_2$ surface next to the air or vacuum as schematically shown in Fig. 10. And the band bending across the SiO$_2$ due to these interfacial charges can be expressed based on poisson function as

$$\Delta E = \frac{Q_{SiO2, Si}}{2 \varepsilon_0 \varepsilon_{SiO2}} T_{SiO2} = -0.0018 T_{SiO2}$$

(5)

From equation (5) we can obtain that the band bending for 4.5 nm, 6.0 nm and 8.0 nm SiO$_2$ is 0.0081 eV, 0.0108 eV and 0.0144 eV, respectively. Larger upward band bending indicates smaller core-level binding energy in SiO$_2$ as shown in Figure 10. These mean that when the SiO$_2$ increases from 4.5 nm to 6.0 nm, the core-level binding energy in SiO$_2$ decreases 0.0108-0.0081=0.0027 eV. From Figure 10 it can be seen that the decrease of core-level binding energy in SiO$_2$ is equal to the changes of $\Delta S_{Si_2p}$ value. So the $\Delta S_{Si_2p}$ decreases 0.0027 eV when the SiO$_2$ increases from 4.5 nm to 6.0 nm. Similarly when the SiO$_2$ increases from 6.0 nm to 8.0 nm, the core-level binding energy in SiO$_2$ decreases 0.0144-0.0108=0.0036 eV. In other word, the $\Delta S_{Si_2p}$ decreases 0.0036 eV. In the previous experimental data, the $\Delta S_{Si_2p}$ changes $\sim 0.05$ eV, 10 times larger than the value induced by areal charges at SiO$_2$/Si interface. Thus it can be concluded that the $\Delta S_{Si_2p}$ variation induced by areal charges at SiO$_2$/Si interface is rather small and thus...
FIGURE 10. Schematic diagram of band structure for the effect of the charges at SiO$_2$/Si interface on the band bending of SiO$_2$/Si stack as a function of SiO$_2$ thickness. The BE expresses the binding energy, and the BE means the decrease of binding energy of Si 2p core-level of SiO$_2$.

can be ignored. As a result, the effect of charge distribution across the SiO$_2$/Si stack can be ruled out.

F. GAP STATES ON THE SiO$_2$ SURFACE AS THE ORIGIN OF THIS SiO$_2$ THICKNESS DEPENDENCE OF BAND ALIGNMENT OF SiO$_2$/Si STACK

Based on the above discussions, we can see that the initial state effect, the final state effect and the charging effect have been all excluded as the origin of this SiO$_2$ thickness dependence of band alignment of SiO$_2$/Si stack, as well as the charge distribution across the SiO$_2$/Si stack. These indicate that there is some or other mechanism for this interesting phenomenon. Here we consider the gap state theory for this phenomenon.

Here the concepts of surface or interfacial gap states and charge neutrality level (CNL) are employed based on the outstanding work by Tersoff, Mönch and Robertson [30]–[35]. Due to finite thicknesses of SiO$_2$ and Si substrate in the SiO$_2$/Si stack, the solutions of Schrödinger’s equation with complex wave vectors become of physical relevance for energies within band gaps, resulting in gap states on the surface of SiO$_2$ and at SiO$_2$/Si interface. These surface or interfacial gap states are derived from the virtual gap states of the complex band structure of the semiconductor or dielectrics, and they may arise from intrinsic, defect or structure induced gap states. They consist of valence- and conduction-band states. The characters of these gap states change across the band gap from predominately donor- to acceptor-like closer to the valence band top and the conduction band bottom, respectively. The energy at which their character changes is called their branch point, or most generally, CNL [33]. The CNL plays a role similar to Fermi level. The Fermi levels of SiO$_2$/Si stack are consistent when the system is in thermodynamic equilibrium. The alignment of Fermi levels of SiO$_2$ and Si substrate is built by charge transfer between the surface gap states on the surface of SiO$_2$ and space charges in Si substrate. Here the interfacial gap states at SiO$_2$/Si interface are not considered because of their rather small density in the range of $10^{10} \sim 10^{11}$ cm$^{-2}$, evaluated by the C-V curve shown in the Figure 8.

Here we consider the case of CNL of SiO$_2$ surface gap states lower than the Fermi level of Si substrate before their contact as shown in the Figure 11(a). Then after their contact electrons will transfer from Si substrate to the surface gap states of SiO$_2$ as shown in Figure 11(a). An upward band bending appears toward the SiO$_2$ surface due to the potential distribution induced by the transferred electrons as shown in Figure 11(b). When the SiO$_2$ thickness increases, more potential drop occurs across the SiO$_2$ in order to align the CNL of SiO$_2$ surface gap states to the bulk Fermi level of Si substrate. As previously described in the Section 3.5, more upward band bending across SiO$_2$ induces smaller binding energy difference between SiO$_2$ and Si substrate. As a result, our experimental results can be well explained by the gap state theory. More details can be referred to our previous work [12].

G. ON THE DEPENDENCE OF BAND ALIGNMENT OF SiO$_2$/Si STACK ON SiO$_2$ THICKNESS: INTRINSIC!

Based on the above discussion, it can be concluded that the dependence of the band alignment of SiO$_2$/Si stack on the
SiO$_2$ thickness is intrinsic. And it is due to the appearance of the gap states on the SiO$_2$ surface. The gap states occur at hetero-junctions which is SiO$_2$/air or SiO$_2$/vacuum interface here. It is an intrinsic characteristic of the SiO$_2$/Si stack. Thus the dependence of the band alignment of SiO$_2$/Si stack on the SiO$_2$ thickness is intrinsic.

The band alignment of SiO$_2$/Si stack can be tuned by the extrinsic effect such as introduction of defect on the SiO$_2$ surface, adsorbate or structure reconstruction, etc., because the characteristics of gap states on the SiO$_2$ surface and their distribution can be affected by the defect, adsorbate or structure reconstruction on the SiO$_2$ surface. And the location of CNL of the gap states on the SiO$_2$ surface can be changed. In our experiments, the CNL of the gap states on the SiO$_2$ surface is lower than the bulk Fermi level of Si. So the electrons transfer from Si to SiO$_2$. If we tune the CNL by the above methods and make it higher than the Fermi level of Si substrate, then electrons transfer from SiO$_2$ to Si. As a result, the band alignment of SiO$_2$/Si stack can be tuned by extrinsic factors. Furthermore, this manuscript indirectly confirms the appearance of gap states on the SiO$_2$ surface.

H. ON THE GAP STATE THEORY ACCOUNTING FOR THE HETERO-STRUCTURE CONTACT

This paper further validates the feasibility of the gap state model in accounting for the band alignment of the hetero-structure contact. Our proposed explanation is an extension of the concepts of the gap state and CNL, which are initially used in discussing the energy band structures of metal/semiconductor contact or metal/insulator contact. The metal induced gap states (MIGS) is usually used to interpret these concepts [36]–[38]. A similar approach for contact between two semiconductors or between semiconductor and insulator is proposed by using CNL in analogy with Fermi level [31], [39], [40]. The SiO$_2$ dielectrics can be regarded as wide band gap semiconductors. Naturally, we can employ the gap states and CNL to describe and determine the energy band lineup for oxide/semiconductor contact. A little difference is that the surface gap states on the SiO$_2$ surface should be also considered. The basic principle, however, is similar. The difference between the Fermi level and CNL is the driving force for charge transfer. Potential drop across the stack is induced in order to align the Fermi levels and make the whole stack in thermodynamic equilibrium. The explanation of the XPS results by the gap state model further confirms the rationality of fundamental theory based on gap states on discussing the band alignments of metal/semiconductor, metal/oxide, semiconductor/semiconductor, and oxide/semiconductor contacts, as well as oxide/oxide contact.

IV. CONCLUSION

The band alignment of SiO$_2$/Si stack with different SiO$_2$ thicknesses is investigated by XPS with and without electron-compensation. It is found that the charging effect can affect the band lineup of SiO$_2$/Si structure when electron-compensation technology is not employed. The relative binding energy distance between core-levels, however, can survive and be accurately determined by XPS with electron-compensation technology. This provide an insight into the precise determination of band offset at oxide hetero-junction excluding the charging effect. With the electron-compensation technology during the XPS measurements, the band alignment of SiO$_2$/Si stack is found to be SiO$_2$ thickness dependent. And this SiO$_2$ thickness dependence is attributed to the gap states on the SiO$_2$ surface. Thus the dependence of band lineup of SiO$_2$/Si stack on SiO$_2$ thickness is intrinsic because of the intrinsic nature of the gap states on SiO$_2$ surface. These further confirm the feasibility of gap state theory in explaining the band lineup at hetero-structures.

REFERENCES

[1] P. Li, Z. Chen, P. Yao, F. Zhang, J. Wang, Y. Song, and X. Zuo, “First-principles study of defects in amorphous-SiO$_2$/Si interfaces,” Appl. Surf. Sci., vol. 483, pp. 231–240, Jul. 2019, doi: 10.1016/j.apsusc.2019.03.216.
[2] Y.-Y. Liu, F. Zheng, X. Jiang, J.-W. Luo, S.-S. Li, and L.-W. Wang, “Ab Initio investigation of charge trapping across the crystalline-Si–amorphous-SiO$_2$ interface,” Phys. Rev. A, Gen. Phys., vol. 11, no. 4, Apr. 2019, Art. no. 044058, doi: 10.1103/PhysRevApplied.11.044058.
[3] R. H. Browning, M. A. Sobolewski, and C. R. Helms, “Effect of electrostatic screening on energy positions of electron spectra near SiO$_2$/Si interfaces,” Phys. Rev. B. Condens. Matter, vol. 38, no. 18, pp. 13407–13410, 1988, doi: 10.1103/PhysRevB.38.13407.
[4] S. Iwata and A. Ishizaka, “Electron spectroscopic analysis of the SiO$_2$/Si system and correlation with metal–oxide–semiconductor device characteristics,” J. Appl. Phys., vol. 79, no. 9, pp. 6653–6713, 1996, doi:10.1063/1.362676.
[5] F. J. Grunthaner, P. J. Grunthaner, R. P. Vasquez, B. F. Lewis, J. Maserjian, and A. Madhukar, “High-resolution X-ray photoelectron spectroscopy as a probe of local atomic structure: Application to amorphous SiO$_2$ and the Si-SiO$_2$ interface,” Phys. Rev. Lett., vol. 43, no. 22, pp. 1683–1686, 1979, doi: 10.1103/PhysRevLett.43.1683.
[6] G. Hollinger, “Structures chimique et electronique de l’interface SiO$_2$–Si,” Appl. Surf. Sci., vol. 8, no. 3, pp. 318–336, 1981, doi: 10.1016/0169-4332(81)90126-4.
[7] K. Z. Zhang, J. N. Greeley, M. M. Banaszak Holl, and F. R. McFeely, “The role of extra-atomic relaxation in determining Si 2p binding energy shifts at silicon/silicon oxide interfaces,” J. Appl. Phys., vol. 82, no. 5, pp. 2499–2503, 1997, doi: 10.1063/1.366037.
[8] A. Pasquarello, M. S. Hybertsen, and R. Car, “Theory of Si 2p core-level shifts at the Si(001)-SiO$_2$ interface,” Phys. Rev. B, Condens. Matter, vol. 53, no. 16, pp. 10492–10495, 1996, doi:10.1103/PhysRevB.53.10492.
[9] Y. Tao, Z. H. Lu, M. J. Graham, and S. P. Tay, “X-ray photoelectron spectroscopy and X-ray absorption near-edge spectroscopy study of SiO$_2$/Si(100),” J. Vac. Sci. Technol. B, vol. 12, no. 4, p. 2500, 1994, doi:10.1116/1.587791.
[10] H. Kobayashi, T. Kubota, H. Kawa, Y. Nakato, and M. Nishiyama, “Oxide thickness dependence of energy shifts in the Si 2p levels for the SiO$_2$/Si structure, and its elimination by a palladium overlay,” Appl. Phys. Lett., vol. 73, no. 7, pp. 933–935, Aug. 1998, doi: 10.1063/1.122042.
[11] A. Iqbal, J. C. W. Bates, and J. W. Allen, “Electron spectroscopy study of the Si-O bonding and the polarization screening near the Si–SiO$_2$ interface,” Appl. Phys. Lett., vol. 47, no. 10, pp. 1064–1066, 1985, doi: 10.1063/1.96380.
[12] X. Wang, “A possible origin of core-level shift in SiO$_2$/Si stacks,” Appl. Phys. Lett., vol. 102, no. 4, Jan. 2013, Art. no. 041603, doi:10.1063/1.4790157.
[13] C. C. Fulton, G. Luovcys, and R. J. Nemaniich, “Electronic properties of the Zr–ZrO$_2$–SiO$_2$–Si(100) gate stack structure,” J. Appl. Phys., vol. 99, no. 6, Mar. 2006, Art. no. 063708, doi: 10.1063/1.2181282.
[14] Z. Q. Liu, S. Y. Chiam, W. K. Chim, J. S. Pan, and C. M. Ng, “Effects of thermal annealing on the band alignment of lanthanum aluminate on silicon investigated by X-ray photoelectron spectroscopy,” J. Appl. Phys., vol. 106, no. 1, Nov. 20090, Art. no. 103718, doi: 10.1063/1.3206453.
[1] E. Bersch, M. Di, S. Consiglio, R. D. Clark, G. J. Leusink, and A. C. Diebold, “Complete band offset characterization of the HfO2/SiO2/Si stack using charge corrected X-ray photoelectron spectroscopy,” J. Appl. Phys., vol. 107, no. 4, Feb. 2010, Art. no. 043702, doi: 10.1063/1.3428967.

[2] M. Di, E. Bersch, R. D. Clark, S. Consiglio, G. J. Leusink, and A. C. Diebold, “Systematic study of the effect of La2O3 incorporation on the flatband voltage and Si band bending in the Ti/HfO2/SiO2/Si stack,” J. Appl. Phys., vol. 108, no. 11, Dec. 2010, Art. no. 114107, doi: 10.1063/1.3516483.

[3] M. Perego and G. Seguini, “Charging phenomena in dielectric/semiconductor heterostructures during X-ray photoelectron spectroscopy measurements,” J. Appl. Phys., vol. 110, no. 5, Sep. 2011, Art. no. 053711, doi: 10.1063/1.3624757.

[4] X. Wang, “Reexamination of band offset transition employing oxide heterojunctions,” Appl. Phys. Lett., vol. 102, no. 3, Jan. 2013, Art. no. 031605, doi: 10.1063/1.4789392.

[5] Y. Hagimoto, T. Fujita, K. Ono, H. Fujikura, M. Oshima, K. Hirose, and M. Tajima, “Characterization of carrier-trapping phenomena in ultrathin chemical oxides using X-ray photoelectron spectroscopy time-dependent measurements,” Appl. Phys. Lett., vol. 74, no. 14, pp. 2011–2013, Apr. 1999, doi: 10.1063/1.123730.

[6] Y. Hagimoto, H. Fujikura, M. Oshima, and K. Hirose, “Characterizing carrier-trapping phenomena in ultrathin SiO2 films by using the X-ray photoelectron spectroscopy time-dependent measurements,” Appl. Phys. Lett., vol. 77, no. 25, pp. 4175–4177, Dec. 2000, doi: 10.1063/1.1334657.

[7] A. Yokozawa and Y. Miyamoto, “First-principles exploration of possible trap terminators in SiO2,” Appl. Phys. Lett., vol. 73, no. 8, pp. 1122–1124, Aug. 1998, doi: 10.1063/1.122103.

[8] K. Hirose, K. Sakano, K. Takahashi, and T. Hattori, “Characterization of SiO2/Si interfaces by using X-ray photoelectron spectroscopy time-dependent measurement,” Surf. Sci., vol. 507–510, pp. 906–910, Jun. 2002.

[9] K. Hirose, “XPS time-dependent measurement of SiO2/Si and HfAlOx/Si interfaces,” J. Electron Spectrosc. Rel. Phenomena, vol. 176, nos. 1–3, pp. 46–51, Jan. 2010, doi: 10.1016/j.elspec.2009.06.003.

[10] K. Choi, H.-C. Wen, G. Bersuker, R. Harris, and B. H. Lee, “Mechanism of flatband voltage roll-off studied with Al2O3 film deposited on terraced oxide,” Appl. Phys. Lett., vol. 93, no. 13, Sep. 2008, pp. 133506–133506, doi: 10.1063/1.2993335.

[11] X. Wang, “Comprehensive understanding of the effect of electric dipole at high-k/SiO2 interface on the flatband voltage shift in metal–oxide–semiconductor device,” Appl. Phys. Lett., vol. 97, no. 6, Aug. 2010, Art. no. 062901, doi: 10.1063/1.3475774.

[12] Y. T. Hou, F. F. Yen, P. F. Hsu, V. S. Chang, P. S. Lim, C. L. Hung, L. G. Yao, J. C. Jiang, H. J. Lin, Y. Jin, S. M. Jang, H. J. Tao, S. C. Chen, and M. S. Liang, “High performance tantalum carbide metal gate stacks for nMOSFET application,” in IEDM Tech. Dig., Dec. 2005, pp. 31–34, doi: 10.1109/IEDM.2005.1609258.

[13] X. Wang, “Band alignment of HfO2 on SiO2/Si structure,” Appl. Phys. Lett., vol. 100, no. 12, Mar. 2012, Art. no. 122907, doi: 10.1063/1.3694274.

[14] W. Wang, W. Mizubayashi, K. Akiyama, T. Nabatame, and A. Toriumi, “Systematic investigation on anomalous positive Vfb shift in Al-incorporated high-k gate stacks,” Appl. Phys. Lett., vol. 92, no. 16, Apr. 2008, Art. no. 1629018, doi: 10.1063/1.2903102.

[15] W. Wang, K. Akiyama, W. Mizubayashi, T. Nabatame, H. Ota, and A. Toriumi, “Effect of Al-diffusion-induced positive flatband voltage shift on the electrical characteristics of Al-incorporated high-k metal-oxide-semiconductor field-effect transistor,” J. Appl. Phys., vol. 105, no. 6, Mar. 2009, Art. no. 064108, doi: 10.1063/1.3093892.

[16] J. Tersoff, “Schottky barrier heights and the continuum of gap states,” Phys. Rev. Lett., vol. 52, no. 6, Apr. 1984, pp. 465–468, doi: 10.1103/PhysRevLett.52.465.

[17] J. Tersoff, “Theory of semiconductor heterojunctions: The role of quantum dipoles,” Phys. Rev. B, Condens. Matter, vol. 30, no. 8, pp. 4874–4877, Oct. 1984, doi: 10.1103/PhysRevB.30.4874.

[18] P. Mönch, “On the electric-dipole contribution to the valence-band offsets in semiconductor-oxide heterostructures,” Appl. Phys. Lett., vol. 91, no. 4, Jul. 2007, Art. no. 042117, doi: 10.1063/1.2760176.

[19] P. W. Peacock and J. Robertson, “Band offsets and Schottky barrier heights of high dielectric constant oxides,” J. Appl. Phys., vol. 92, no. 8, pp. 4712–4721, Oct. 2002, doi: 10.1063/1.1506388.

[20] J. Robertson and B. Falabretti, “Band offsets of high K gate oxides on III-V semiconductors,” J. Appl. Phys., vol. 100, no. 1, 2006, Art. no. 014111, doi: 10.1063/1.2121370.

[21] V. Heine, “Theory of surface states,” Phys. Rev., vol. 138, no. 6A, pp. A1689–A1696, Jun. 1965, doi: 10.1103/PhysRev.138.A1689.

[22] S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, “Ionicity and the theory of Schottky barriers,” Phys. Rev. B, Condens. Matter, vol. 15, no. 4, pp. 2154–2162, Feb. 1977, doi: 10.1103/PhysRevB.15.2154.

[23] C. Tejedor, F. Flores, and E. Louis, “The metal-semiconductor interface: Si (111) and zinclende (110) junctions,” J. Phys. C, Solid State Phys., vol. 10, no. 12, p. 2163, 1977, doi: 10.1088/0022-3719/10/12/002.

[24] J. Robertson and C. W. Chen, “Schottky barrier heights of tantalum oxide, barium strontium titanate, lead titanate, and strontium bismuth tantalate,” Appl. Phys. Lett., vol. 74, no. 8, pp. 1168–1170, Feb. 1999, doi: 10.1063/1.123476.

[25] J. Robertson, “Band offsets of wide-band-gap oxides and implications for future electronic devices,” J. Vac. Sci. Technol. B, Microelectron. Nanometer Struct., vol. 18, no. 3, p. 1785, 2000.

**YONGGUI XU** received the master’s degree in semiconductor physics from the Wuhan University of Technology, Wuhan, China, in 2006. He is currently with Weifang University as an Associate Professor, and his research interest is in advanced materials included in semiconductor devices.

**KAI HAN** received the Ph.D. degree in electronic engineering from the University of Chinese Academy of Sciences, Beijing, China, in 2013. He joined Weifang University, in 2013, and became an Associate Professor, in January 2017. His research field is materials using in microelectronic devices.

**JINJUAN XIANG** received the Ph.D. degree in electronic engineering from the University of Chinese Academy of Sciences, Beijing, China, in 2016, and she is currently with the Institute of Microelectronics, Chinese Academy of Sciences, Beijing, China. She is currently engaged in the research and development on atomic layer deposition, especially on high-k and metal gate materials for Nano CMOS applications.

**XIAOLEI WANG** (Member, IEEE) received the Ph.D. degree in electronic engineering from the University of Chinese Academy of Sciences, Beijing, China, in 2013. He became an Associate Professor with the Institute of Microelectronics, Chinese Academy of Sciences, in January 2016. He is currently engaged in research of mobility characteristics of Ge MOSFETs.