

Received June 30, 2020, accepted August 13, 2020, date of publication August 28, 2020, date of current version September 11, 2020.

Digital Object Identifier 10.1109/ACCESS.2020.3020072

On the Dependence of Band Alignment of SiO₂/Si Stack on SiO₂ Thickness: Extrinsic Or Intrinsic?

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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 SiO₂/Si stack on SiO₂ thickness is restudied. The band structure of SiO₂/Si stack is investigated by time-dependent X-ray photoelectron spectroscopy (XPS) with and without electron-compensation technology. The binding energy difference ΔSi_{2p} between Si 2p core-levels of SiO₂ and Si, measured without electron-compensation, is found larger than that with electron-compensation, owing to the charging effect. And more severe charging effect induces larger ΔSi_{2p} . The ΔSi_{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 SiO₂/Si stack is found to be SiO₂ thickness dependent. And this dependence is attributed to the gap states on the SiO₂ surface and their lower charge neutrality level than the Fermi level of Si substrate, resulting in electron transfer from Si to SiO₂ and electric potential distribution across the SiO₂. As a result, the experimentally obtained dependence of ΔSi_{2p} on SiO₂ 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, SiO₂/Si stack, XPS.

I. INTRODUCTION

Complete understanding of electronic structure and band alignment of SiO₂/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 SiO₂ thickness, or namely the binding energy difference ΔSi_{2p} between Si 2p core-levels of SiO₂ 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 SiO₂ 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 H₈Si₈O₁₂ cluster, i.e., all Si atoms in SiO₂ were with same Si–O ring size, strain, stoichiometry and crystallinity regardless of the SiO₂ thickness. And they found that the band alignment of SiO₂/Si structure was still SiO₂ 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 SiO₂/Si interface using pseudopotential approach, and found that structural deformations such as those implied by the distribution of Si–O bond lengths in amorphous SiO₂ yielded distributions of core-level shifts that were too small to account for the observed dependence of band alignment of SiO₂/Si structure on the SiO₂ 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.

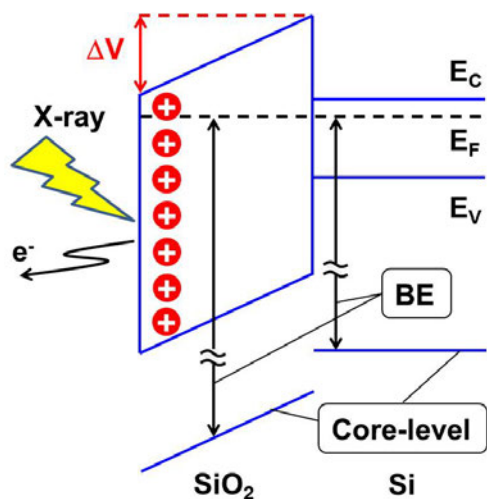


FIGURE 1. Schematic diagram of energy band of SiO₂/Si stack under X-ray irradiation. The positive charges are induced with most of the induced charges near the surface region of SiO₂ film. These positive charges induce potential drop across the SiO₂ and subsequent downward energy band bending on the surface of SiO₂. The ΔV expresses the potential drop due to X-ray induced positive charges, and BE means binding energy.

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 ΔSi_{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 ΔSi_{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 ΔSi_{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 ΔSi_{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 ΔSi_{2p} is induced when there is no electron-compensation compared to the value with electron-compensation, i.e., charging effect induces larger ΔSi_{2p} . Then the influence of charging effect is quantitatively evaluated. And it is found that the binding energy difference ΔSi_{2p} is scarcely affected by negative charging effect when electron-compensation technique is used even though positive charging effect shows an 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 4f_{7/2}, Ag 3d_{5/2}, and Cu 2p_{3/2} 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 2p_{1/2} to Si 2p_{3/2}.

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 thicknesses being 4.5 nm, 6.0 nm and 8.0 nm and/or 20 nm. Then 5 nm TiN and 75 nm W were deposited on the SiO₂ by atomic layer deposition (ALD). After the removal of backside native SiO₂, 700 nm Al was deposited on the backside by physical vapor deposition (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 (V_{FB}) 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

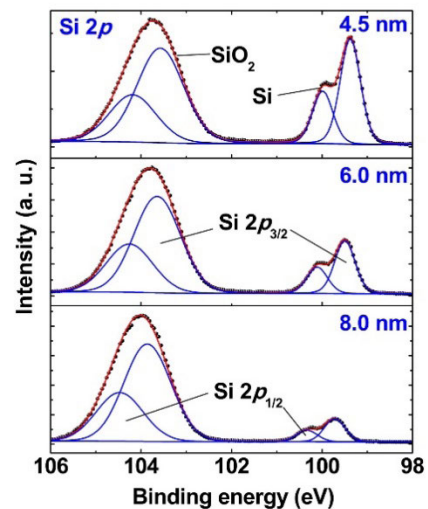


FIGURE 2. XPS spectra of Si 2p core-level for 4.5-nm-SiO₂/Si stack, 6.0-nm-SiO₂/Si stack, and 8.0-nm-SiO₂/Si stack. The electron-compensation technique is employed during the XPS measurements. In addition, the spectra are given without any calibration such as setting C 1s core-level, and are shown using the raw data given by the XPS tool.

TABLE 1. Summary of core-level binding energy by fitting the spectra in Figs. 2 and 3.

Thickness of SiO ₂ (nm)	Binding energy of core-level (eV)		
	Si 2p _{3/2} of Si substrate	Si 2p _{3/2} of SiO ₂	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

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 2p_{3/2} core-level obtained by fitting the spectra in Figure 2 are summarized in Table 1.

We can use 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

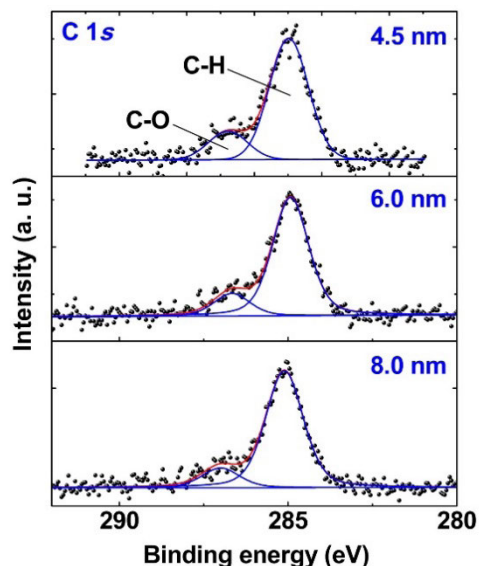


FIGURE 3. XPS spectra of C 1s core-level for 4.5-nm-SiO₂/Si stack, 6.0-nm-SiO₂/Si stack, and 8.0-nm-SiO₂/Si stack. Similar to the case in Fig. 2, there is electron-compensation during the XPS measurements.

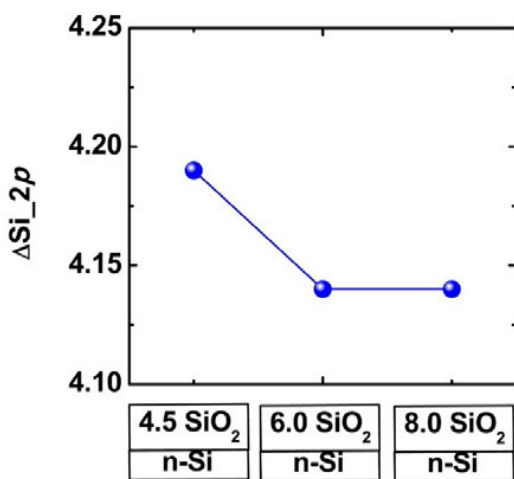


FIGURE 4. The ΔSi_{2p} of SiO₂/Si stack as a function of SiO₂ thickness when the electron-compensation technique is used during the XPS measurements.

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

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. Owing 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

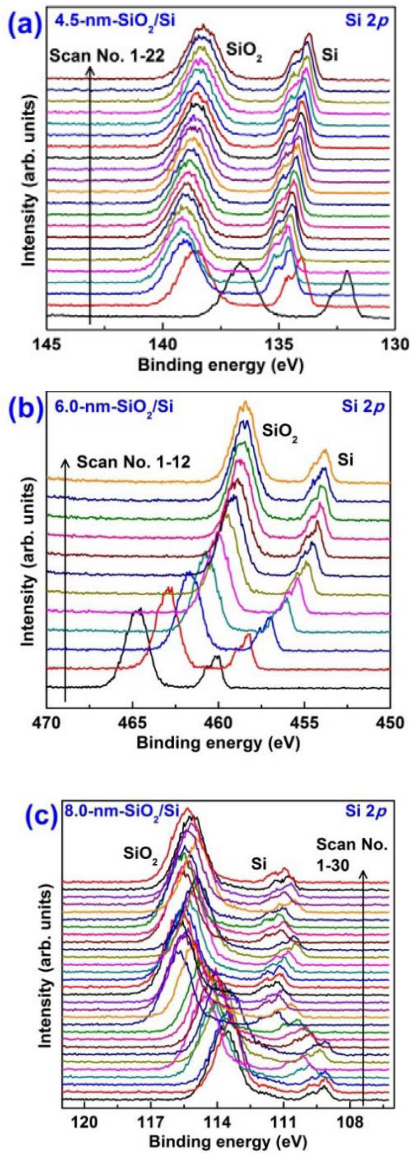


FIGURE 5. XPS spectra of Si 2p core-levels as a function of X-ray irradiation time under the mode without electron-compensation for (a) 4.5-nm-SiO₂/Si stack, (b) 6.0-nm-SiO₂/Si stack, and (c) 8.0-nm-SiO₂/Si stack. Here the X-ray irradiation time is equally expressed by the scanning number, with large scanning number corresponding to longer X-ray irradiation time. It should be noted that the first scan of the spectrum in Figure 5(b) corresponds to the time of 120 min after the X-ray irradiation. The scan No. in Figure 5(a)-(c) does not correspond to the same measurement time.

both peak position and shape. Figure 6(b) shows the Si 2p core-level binding energy and the ΔSi_{2p} as a function of X-ray irradiation time for 6.0-nm-SiO₂/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 SiO₂/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 ΔSi_{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

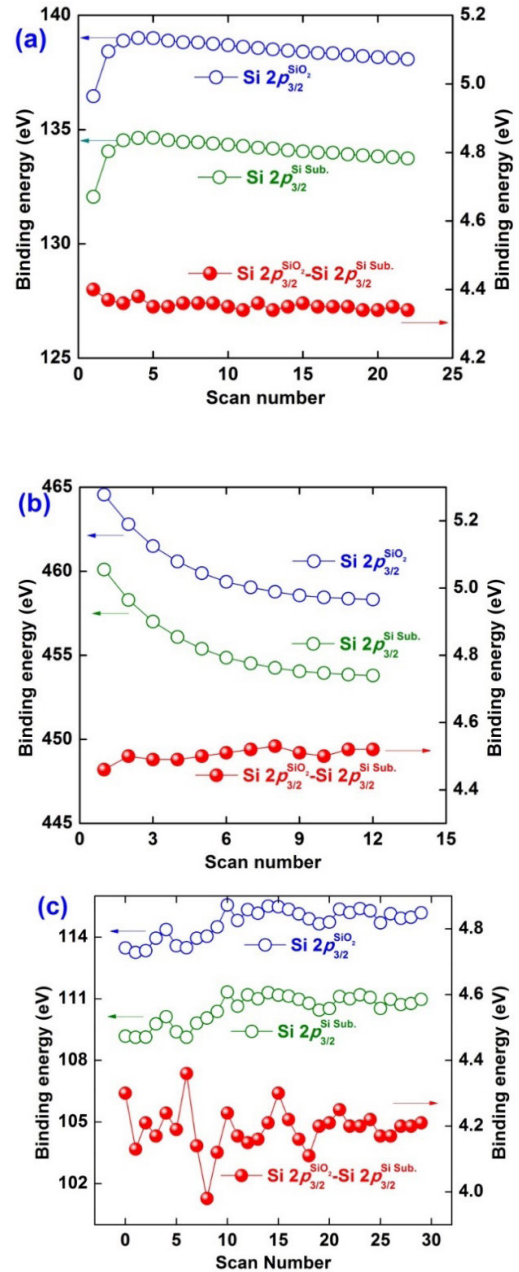


FIGURE 6. The Si 2p core-level binding energy and the ΔSi_{2p} as a function of X-ray irradiation time for (a) 4.5-nm-SiO₂/Si stack, (b) 6.0-nm-SiO₂/Si stack, and (c) 8.0-nm-SiO₂/Si stack.

binding energy of 8.0-nm-SiO₂/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 ΔSi_{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-SiO₂/Si stack in Figure 6(a) or 6(b) may be related with some SiO₂ thickness dependent characteristic, which needs further investigation. Fortunately these do not affect the evaluation of the charging effect.

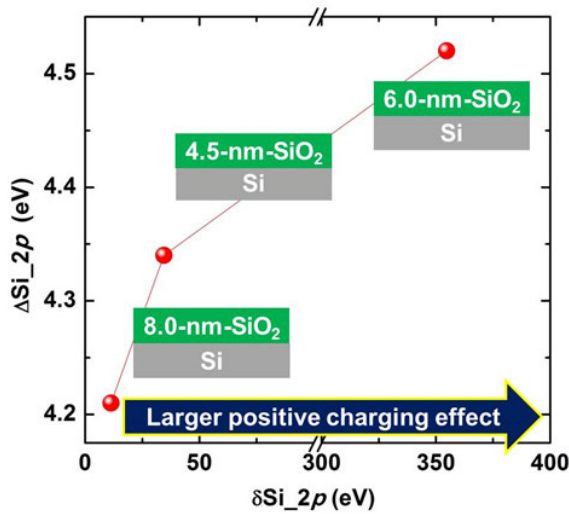


FIGURE 7. The ΔSi_{2p} as a function of the Si 2p core-level shift δSi_{2p} . The schematic sample structures indicate which stack the data of ΔSi_{2p} and δSi_{2p} come from.

C. QUANTITATIVE EVALUATION OF THE INFLUENCE OF CHARGING EFFECT ON THE ΔSi_{2p}

Figure 7 shows the ΔSi_{2p} as a function of the Si 2p core-level shift δSi_{2p} , which is defined as the difference between the Si 2p core-level binding energies for SiO₂ without and with electron-compensation technique. It can be seen that larger δSi_{2p} or namely more severe charging effect, induces larger ΔSi_{2p} . A linear fitting of the data in Figure 7 gives a decrease of 7.6-56 meV for ΔSi_{2p} per decrease of 10 eV for δSi_{2p} . Even though the linear fitting makes no physical sense, it can approximately evaluate the variation trend. When the extend of charging effect δSi_{2p} is ~11 eV, the ΔSi_{2p} is ~4.20 eV, as shown in Fig. 7. As a results, when δSi_{2p} decreases to be 0 eV the ΔSi_{2p} is approximately calculated to be 4.15-4.19 eV, which is identical to the value of ΔSi_{2p} with electron-compensation (4.14-4.19 eV for 4.5~8.0-nm-SiO₂/Si stack). So it can be concluded that the ΔSi_{2p} is obtained accurately when the electron-compensation is employed during the XPS measurements.

Then the charging effect on the relative distance between core-levels or ΔSi_{2p} is approximately and quantitatively estimated. Based on a capacitor approximation, the Si 2p core-level binding energy shift δSi_{2p} induced by charging effect in the XPS measurements by the Thermo Scientific ESCALAB 250Xi without electron-compensation can be expressed as follows[18]:

$$\delta Si_{2p} = \frac{eN}{2\epsilon_0} d_0 \tag{1}$$

where e is the electron charge. N is the effective charge density per unit of area induced by the charging effect. The ϵ_0 is the vacuum permittivity. The d_0 is the photoelectron effective escaping distance from sample to electron collection lens of the spectrometer and it is assumed to be approximately 60.0 μ m here (one tenth of the X-ray beam diameter of

650 μ m used in this experiment). From the equation (1) we can obtain the X-ray irradiation induced charges as follows:

$$N = \frac{2\epsilon_0}{ed_0} \delta Si_{2p} \tag{2}$$

The variation of binding energy difference between core-levels of SiO₂ and Si substrates ΔSi_{2p} , induced by this effective charge density per unit of area, is approximately given by

$$\Delta \delta Si_{2p} = \frac{eN}{2\epsilon_0} d_{oxide} = \frac{d_{oxide}}{d_0} \delta Si_{2p} \tag{3}$$

where the d_{oxide} expresses the SiO₂ oxide thickness. Then based on equation (3) it can be obtained that for SiO₂ thickness of 6 nm, the δSi_{2p} of 10 eV corresponds to the ΔSi_{2p} of 1 meV, which is approximately consistent with the experimental results of 7.6-56 meV for ΔSi_{2p} per 10 eV for δSi_{2p} . The deviation maybe come from the exact value of d_0 . All of these show that the δSi_{2p} of less than 10 eV has a nearly negligible effect on the accurate value of ΔSi_{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 ~99-103 eV when the electron-compensation technique was employed, indicating that the influence of charging effect on ΔSi_{2p} is so weak that it can be ignored reasonably. Thus the binding energy difference between core-levels are accurately obtained without any charging effect when the electron-compensation technique is employed during the XPS measurements.

D. THE EXCLUSION OF THE CHARGING EFFECT ACCOUNTING FOR THE SiO₂ THICKNESS DEPENDENCE OF BAND ALIGNMENT OF SiO₂/Si STACK

As shown in the previous section, the binding energy difference ΔSi_{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 ΔSi_{2p} value. Based on the experimental results in Sec. 3.1, the band alignment of SiO₂/Si stack still shows SiO₂ thickness dependence when the electron-compensation technology is employed. Thus we can exclude the charging effect as the physical origin of this SiO₂ thickness dependence of band alignment of SiO₂/Si stack in our experiments.

E. THE EXCLUSION OF INTERFACIAL OR BULK CHARGE DISTRIBUTION ACROSS THE SiO₂/Si STACK ACCOUNTING FOR THE SiO₂ THICKNESS DEPENDENCE OF BAND ALIGNMENT OF SiO₂/Si STACK

This section discusses the possible effect of charge distribution on the band alignment of SiO₂/Si stack. The charge distribution here means the interfacial (at SiO₂/Si interface) and/or bulk (in SiO₂) charges located in the gate

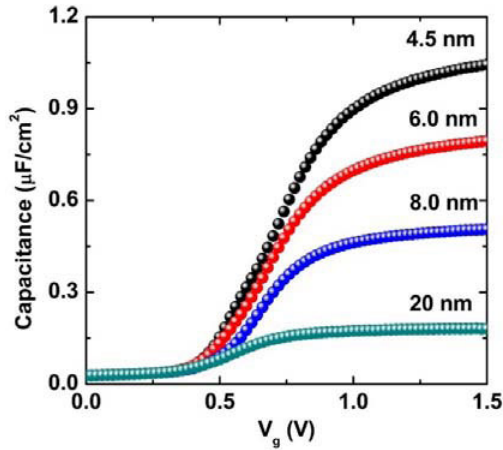


FIGURE 8. The C-V data of TiN/SiO₂/Si capacitors for different SiO₂ thicknesses.

stack but not 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 SiO₂/Si stack needs investigation.

Figure 8 shows the C-V curves of TiN/SiO₂/Si MOS capacitor for different SiO₂ thicknesses. It can be seen that well C-V shape is obtained. Figure 9 shows the flatband voltage (V_{FB}) as a function of SiO₂ thickness (T_{SiO_2}) by fitting the C-V curves in Fig. 8 considering the quantum effect. Then the densities of interfacial charges at SiO₂/Si interface and bulk charges in SiO₂ can be obtained to be $+7.55 \times 10^{10} \text{ \#/cm}^2$ and 0 \#/cm^3 , respectively, by the following formula:

$$V_{FB} = \phi_{ms} - \frac{Q_{SiO_2,Si}}{\epsilon_0 \epsilon_{SiO_2}} T_{SiO_2} - \frac{\rho_{bulk,SiO_2}}{2\epsilon_0 \epsilon_{SiO_2}} T_{SiO_2}^2 \quad (4)$$

where the ϕ_{ms} is the vacuum workfunction difference between TiN and Si substrate. $Q_{SiO_2,Si}$ is the areal charge densities (per unit area) at the SiO₂/Si interface. ρ_{bulk,SiO_2} is the bulk charge densities (per unit volume) in SiO₂. ϵ_0 and ϵ_{SiO_2} express the vacuum permittivity and the relative permittivity of SiO₂, respectively. Then based on Equation (4), it can be seen that the V_{FB} is a quadratic function of T_{SiO_2} , with the linear and quadratic terms determining the values of charges at SiO₂/Si interface and in SiO₂. Also shown in the Fig. 9 is the fitting formula of experimental V_{FB} - T_{SiO_2} data. By comparing this formula with equation (4) we can obtain the charge distribution across the SiO₂/Si stack, i.e., interfacial charges at SiO₂/Si interface and in SiO₂. 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 SiO₂ are rather small and cannot be detected by the experiment. This means that the thermal

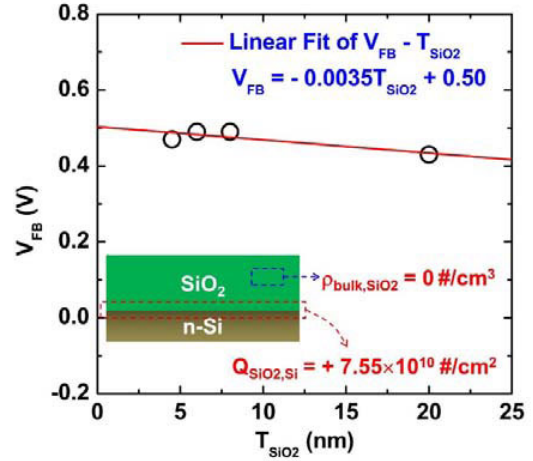


FIGURE 9. The V_{FB} -EOT plot of TiN/SiO₂/Si capacitors for different SiO₂ thicknesses. Also shown in the Figure 9 are the fitting formula and the values of charge distributions across the stack.

oxidation of Si at $\sim 1050 \text{ }^\circ\text{C}$ in our experiments results in high quality SiO₂. The traps in the SiO₂ are rather small and can be ignored.

The charge distribution has no effect on the band alignment of SiO₂/Si stack as a function of SiO₂ thickness. Firstly the effect of bulk charges in SiO₂ is discussed. From the above experimental results it can be seen that the bulk charges in SiO₂ is 0 \#/cm^3 . Thus these charges do not induce electric potential across the SiO₂/Si stack, i.e., no effect on the band alignment of SiO₂/Si stack. Then the effect of interfacial charges at SiO₂/Si interface is evaluated. These positive charges induce upward band bending toward the SiO₂ surface next to the air or vacuum as schematically shown in Fig. 10. And the band bending across the SiO₂ due to these interfacial charges can be expressed based on poisson function as

$$\Delta E = \frac{Q_{SiO_2,Si}}{2\epsilon_0 \epsilon_{SiO_2}} T_{SiO_2} = -0.0018 T_{SiO_2} \quad (5)$$

From equation (5) we can obtain that the band bending for 4.5 nm, 6.0 nm and 8.0 nm SiO₂ is 0.0081 eV, 0.0108 eV and 0.0144 eV, respectively. Larger upward band bending indicates smaller core-level binding energy in SiO₂ as shown in Figure 10. These mean that when the SiO₂ increases from 4.5 nm to 6.0 nm, the core-level binding energy in SiO₂ decreases $0.0108 - 0.0081 = 0.0027 \text{ eV}$. From Figure 10 it can be seen that the decrease of core-level binding energy in SiO₂ is equal to the changes of ΔSi_{2p} value. So the ΔSi_{2p} decreases 0.0027 eV when the SiO₂ increases from 4.5 nm to 6.0 nm. Similarly when the SiO₂ increases from 6.0 nm to 8.0 nm, the core-level binding energy in SiO₂ decreases $0.0144 - 0.0108 = 0.0036 \text{ eV}$. In other word, the ΔSi_{2p} decreases 0.0036 eV. In the previous experimental data, the ΔSi_{2p} changes $\sim 0.05 \text{ eV}$, 10 times larger than the value induced by areal charges at SiO₂/Si interface. Thus it can be concluded that the ΔSi_{2p} variation induced by areal charges at SiO₂/Si interface is rather small and thus

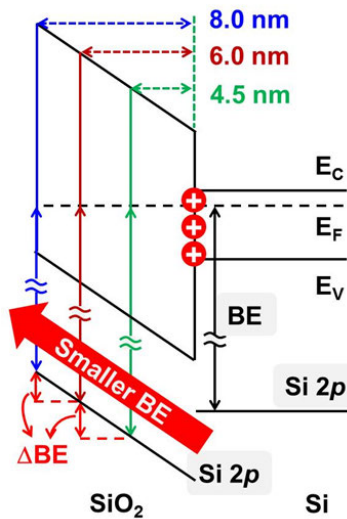


FIGURE 10. Schematic diagram of band structure for the effect of the charges at SiO₂/Si interface on the band bending of SiO₂/Si stack as a function of SiO₂ thickness. The BE expresses the binding energy, and the BE means the decrease of binding energy of Si 2p core-level of SiO₂.

can be ignored. As a results, the effect of charge distribution across the SiO₂/Si stack can be ruled out.

F. GAP STATES ON THE SiO₂ SURFACE AS THE ORIGIN OF THIS SiO₂ THICKNESS DEPENDENCE OF BAND ALIGNMENT OF SiO₂/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 SiO₂ thickness dependence of band alignment of SiO₂/Si stack, as well as the charge distribution across the SiO₂/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 SiO₂ and Si substrate in the SiO₂/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 SiO₂ and at SiO₂/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 SiO₂/Si stack are consistent when the system is in thermodynamic equilibrium. The alignment of Fermi levels of SiO₂ and Si substrate is built by charge transfer between the surface gap

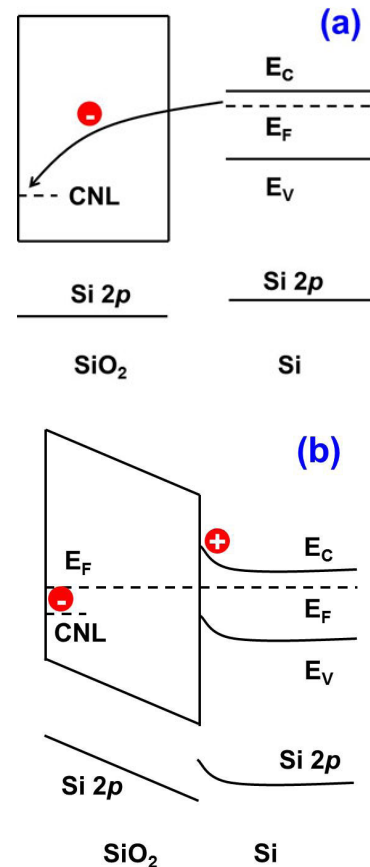


FIGURE 11. Schematic of band structure of SiO₂/Si stack (a) before contact and (b) after contact.

states on the surface of SiO₂ and space charges in Si substrate. Here the interfacial gap states at SiO₂/Si interface are not considered because of their rather small density in the range of 10¹⁰ ~10¹¹ cm⁻², evaluated by the C-V curve shown in the Figure 8.

Here we consider the case of CNL of SiO₂ 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 SiO₂ as shown in Figure 11(a). An upward band bending appears toward the SiO₂ surface due to the potential distribution induced by the transferred electrons as shown in Figure 11(b). When the SiO₂ thickness increases, more potential drop occurs across the SiO₂ in order to align the CNL of SiO₂ surface gap states to the bulk Fermi level of Si substrate. As previously described in the Section 3.5, more upward band bending across SiO₂ induces smaller binding energy difference between SiO₂ 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 SiO₂/Si STACK ON SiO₂ THICKNESS: INTRINSIC!

Based on the above discussion, it can be concluded that the dependence of the band alignment of SiO₂/Si stack on the

SiO₂ thickness is intrinsic. And it is due to the appearance of the gap states on the SiO₂ surface. The gap states occur at hetero-junctions which is SiO₂/air or SiO₂/vacuum interface here. It is an intrinsic characteristic of the SiO₂/Si stack. Thus the dependence of the band alignment of SiO₂/Si stack on the SiO₂ thickness is intrinsic.

The band alignment of SiO₂/Si stack can be tuned by the extrinsic effect such as introduction of defect on the SiO₂ surface, adsorbate or structure reconstruction, etc., because the characteristics of gap states on the SiO₂ surface and their distribution can be affected by the defect, adsorbate or structure reconstruction on the SiO₂ surface. And the location of CNL of the gap states on the SiO₂ surface can be changed. In our experiments, the CNL of the gap states on the SiO₂ surface is lower than the bulk Fermi level of Si. So the electrons transfer from Si to SiO₂. If we tune the CNL by the above methods and make it higher than the Fermi level of Si substrate, then electrons transfer from SiO₂ to Si. As a result, the band alignment of SiO₂/Si stack can be tuned by extrinsic factors. Furthermore, this manuscript indirectly confirms the appearance of gap states on the SiO₂ 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 contacts [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 SiO₂ 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 SiO₂ 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 SiO₂/Si stack with different SiO₂ thicknesses is investigated by XPS with and without electron-compensation. It is found that the charging effect can affect the band lineup of SiO₂/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 SiO₂/Si stack is found to be SiO₂ thickness dependent. And this SiO₂ thickness dependence is attributed to the gap states on the SiO₂ surface. Thus the dependence of band lineup of SiO₂/Si stack on SiO₂ thickness is intrinsic because of the intrinsic nature of the gap states on SiO₂ surface. These further confirm the feasibility of gap state theory in explaining the band lineup at hetero-structures.

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