

Band offsets for ultrathin SiO₂ and Si₃N₄ films on Si(111) and Si(100) from photoemission spectroscopy

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High resolution soft x-ray photoelectron spectroscopy with synchrotron radiation is used to study the interfaces of SiO₂/Si(111), SiO₂/Si(100), Si(111)/Si₃N₄, and SiO₂/Si₃N₄ for device-quality ultrathin gate oxides and nitrides. The thin oxides and nitrides were grown by remote plasma deposition at a temperature of 300 °C. Aftergrowth samples were further processed by rapid thermal annealing for 30 s at various temperatures from 700 to 950 °C. The Si(111)/Si₃N₄ samples were air exposed and formed a thin ~6 Å SiO₂ layer with a Si(2*p*) core-level shift of 3.9 eV, thus allowing us to study both the Si(111)/Si₃N₄ and SiO₂/Si₃N₄ interfaces with a single type of sample. We obtain band offsets of 4.54±0.06 eV for SiO₂/Si(111) and 4.35±0.06 eV for SiO₂/Si(100) with film thicknesses in the range 8–12 Å. The Si(111)/Si₃N₄ nitrides show 1.78±0.09 eV valence-band offset for 15–21 Å films. This value agrees using the additivity relationship with our independent photoemission measurements of the nitride–oxide valence-band offset of 2.66±0.14 eV. However, we measure a substantially larger SiO₂/Si₃N₄ Δ*E*_v value of 3.05 eV for thicker (~60 Å) films, and this indicates substantial differences in core-hole screening for films of different thickness due to additional silicon substrate screening in the thinner (15–21 Å) films. © 1999 American Vacuum Society. [S0734-211X(99)08904-0]

I. INTRODUCTION

Interfaces of SiO₂/Si(111) and SiO₂/Si(100) have been extremely well studied by photoemission spectroscopy^{1–5} but little attention has been given to measurements of the valence-band offsets for ultrathin oxide systems. A crucial issue that continues to inhibit understanding of spectroscopic measurements is sample preparation at the device-grade level of processing such that interface details can be usefully compared to other measurements. In the present study we use ultrathin oxides and nitrides grown on Si(111) and on Si(100) that achieve these interface conditions. Since gate oxide thickness used in current devices has continued to decrease in thickness with corresponding improvements in ox-

ide growth, postgrowth processing and device properties, we decided to reinvestigate the issue of the band offsets for interfaces of SiO₂/Si(111) and SiO₂/Si(100) using current state-of-the-art methods of gate oxide growth. Standard interface capacitance and other electrical measurements done on the same wafer as the electron spectroscopic experiments independently characterized our device-grade samples.^{6–8}

II. EXPERIMENTAL DETAILS

A. Film preparation methods

Native oxide layers on Si(111) substrates were removed by etching in 40 wt % NH₄F for 4 min and then rinsing for 20 s with deionized water. The Si(100) wafers were treated with 1 wt % HF and also rinsed in de-ionized water for 20 s. These steps produced H-terminated Si surfaces. After this

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step, the wafers were loaded into the vacuum chamber. The films were then grown by one of three methods.

1. Method 1

Ultrathin SiO₂ samples were made using remote plasma-enhanced (RPE) oxidation. Wafers of Si(111) or Si(100) were heated to 300 °C and exposed to a flow of excited oxygen formed in a remote He/O₂ rf plasma. The He and O₂ were flowed at 200 and 20 sccm (cm³ min⁻¹), respectively, at a total chamber pressure of 0.3 Torr, with the 13.56 MHz rf plasma power fixed at 30 W. On-line (i.e., *in situ*) Auger electron spectroscopy (AES) measurements characterized the growth rate as following a power law SiO₂ film thickness dependence on time: $t_{\text{ox}} \approx 7t^{0.28}$ (where t_{ox} is the SiO₂ thickness in Å and t is plasma exposure time in minutes).⁹ The SiO₂ films reported in this study [measured by soft x-ray photoelectron spectroscopy (SXPS) to be in the range 9–22 Å] were made using exposure times of approximately 5 s to nearly 10 min.

2. Method 2

Remote plasma-enhanced chemical vapor deposition (RPECVD) of SiO₂ to produce thicker (~80 Å) films. These were produced by flowing dilute silane downstream from the oxygen plasma. After passing the plasma excitation, excited O₂ flowed through a rf ring of 2% SiH₄ in helium. The wafers were found to grow at ~34–40 Å per minute at a wafer temperature of 300 °C. The chamber pressure was maintained at 0.3 Torr during growth. Flow rates were: 200 sccm He, 20 sccm O₂, and 10 sccm of the 2% SiH₄ mixture.

3. Method 3

RPECVD was also used to produce (hydrogen-rich) Si₃N₄ films ranging in thickness from 10 to 80 Å. Excited N₂ from the He plasma was flowed through a ring of SiH₄. The wafers were observed to grow at a rate of ~6–8 Å/min at a wafer temperature of 300 °C. The chamber pressure was maintained at 0.2 Torr during growth. Flow rates were: 200 sccm He, 60 sccm N₂, 10 sccm of the 2% SiH₄ mixture. When these samples were exposed to air, reaction with atmospheric water produced a native silicon oxide overlayer (~5–10 Å thickness), presumably by the substitution reaction:



After growth, some of the samples were subjected to *ex situ* rapid thermal annealing (RTA) using optical heating in an Ar atmosphere. In many cases, a single oxidized wafer was broken *ex situ* and fragments were annealed at various temperatures in the range 600–950 °C by RTA (for 30 s) in Ar, providing a means of comparing “as grown” and annealed samples under the same oxidation conditions.

The films were transferred under air to the ultrahigh vacuum XPS chamber of NSLS-U4A. Once in vacuum, the samples were annealed at ~500 °C by electron-beam heating of the metal sample holder. This removes contamination due to weakly bonded adsorbates picked up in air. The thick

nitride films were further treated with neon ion etching (5 min at 500 eV beam energy, 3×10^{-5} Torr chamber pressure) to remove some of the SiO₂ overlayer. Then, a second ~600 °C anneal was performed after the etching in order to reequilibrate the film somewhat.

B. Soft x-ray photoemission spectroscopy (SXPS) measurements

The SXPS configuration at the U4A beamline of the National Synchrotron Light Source (NSLS) includes a 6 m toroidal grating monochromator which produces a photon beam with ≤ 0.2 eV resolution at photon energies ($h\nu$) of 10–200 eV.^{9,10} At 130 photon energy this system has ~0.15 eV total resolution, photons, and electrons. The photoelectron kinetic energy (KE_e) was measured with a 100 mm hemispherical analyzer fixed at 45° to the photon beam axis. All the spectra presented here were obtained with the sample surface facing the analyzer at the normal emission geometry ($\alpha=90^\circ$ take-off angle). The room temperature SXPS spectra were collected with the sample holder grounded, and the electron analyzer was used in fixed pass energy mode with a resolution of ~0.1 eV.

The Fermi energy E_F was used as the reference energy and was measured using a metal sample attached to the same sample holder. The E_F threshold appeared at a kinetic energy of 4.6 eV less than the photon energy. Valence-band offsets were measured within each spectrum individually and were not affected by any small offset bias applied to the sample. The sample SiO₂ film thickness was estimated from the Si(2*p*) SXPS SiO₂ and substrate peak intensity ratio, as described elsewhere,¹¹ and were consistent with independent *in situ* (on-line) AES and ellipsometric measurements within experimental uncertainties.

III. RESULTS

A. Valence-band offsets for thin SiO₂ films on Si(111) and Si(100)

Because of the surface sensitivity of SXPS, the Si substrate signal can be seen only for thin films. Thus, the Si–SiO₂ valence-band offset ΔE_V was measured using thin RPE oxidation SiO₂ films of 10 ± 2 Å thickness. This film thickness was measured from the core-level peak intensity ratio between Si and SiO₂ Si(2*p*) peaks [binding energy (BE, Si) ~99.3 eV] which are distinct due to the ~4 eV chemical shift difference in BE (SiO₂) ~104 eV. As shown in Fig. 1, the valence band spectra for such films show the same features despite being obtained using different photon energies. The differences can be explained as: (i) Auger transitions which have fixed electron energies, or (ii) intensity changes due to energy-dependent electron escape depths. These spectra are dominated by a signal attributable to oxygen atoms in the SiO₂ film. The O(2*s*) peak at binding energy ($h\nu - \text{KE}$) ~26 eV can clearly be distinguished from the O(2*p*) peak at 7 eV (with additional components at ~11 and 14 eV). The onset of the O(2*p*) signal at BE ~4 eV corresponds to the valence band maximum (E_V) of the SiO₂ film.

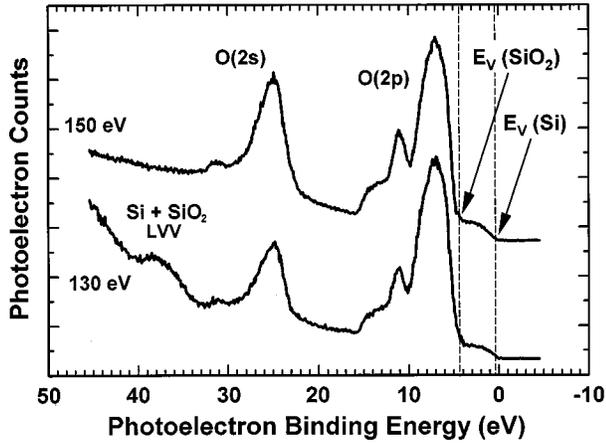


FIG. 1. Typical valence band scans for a thin (~15 Å) SiO₂ film grown on Si(111) substrate. Shown are spectra acquired at 130 and 150 eV photon energy. The higher energy shows more substrate signal (BE < 4 eV) due to increased electron escape depth. The lower energy scan shows greater scattered electron background as well as silicon Auger signal near 90 eV electron kinetic energy. The small peak near 31 eV binding energy is Ta(4f) XPS signal from the tantalum wire which was used to hold the silicon wafer fragment to the sample holder.

The signal at lower binding energy results from the Si substrate, which has an onset BE of nearly zero as shown in Fig. 1.

The difference between these two onsets corresponds directly to the valence-band offset of the interface. That is, $\Delta E_V = E_V(\text{Si}) - E_V(\text{SiO}_2)$. Thus, we have measured ΔE_V by fitting the low-binding-energy part of the spectrum with two broadened step functions. In Fig. 2 is shown the edge region of an SXPS spectra obtained at 130 eV photon energy for a SiO₂ film of 10 Å thickness grown on Si(111). We have found that the spectrum in this region is well modeled by a pair of Gaussian-broadened Fermi functions (the Fermi width is virtually negligible in this case compared with the Gaussian component), with a parabolic peak added to match the signal found experimentally just below the Si band edge.

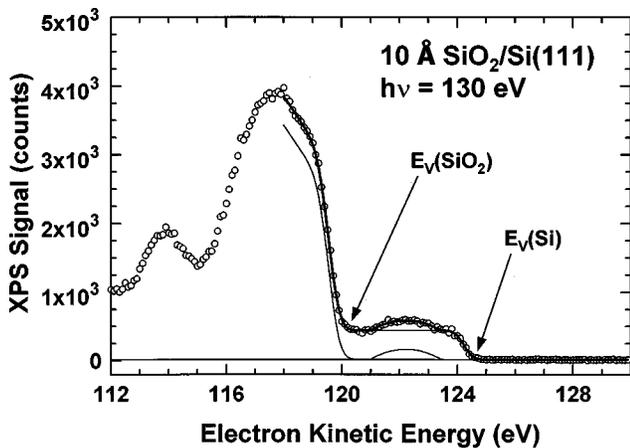


FIG. 2. Closeup view of the silicon and silicon dioxide valence-band edges measured for a 10 Å SiO₂ film grown on Si(111) substrate using a photon energy of 130 eV. The fitting functions are described in the text.

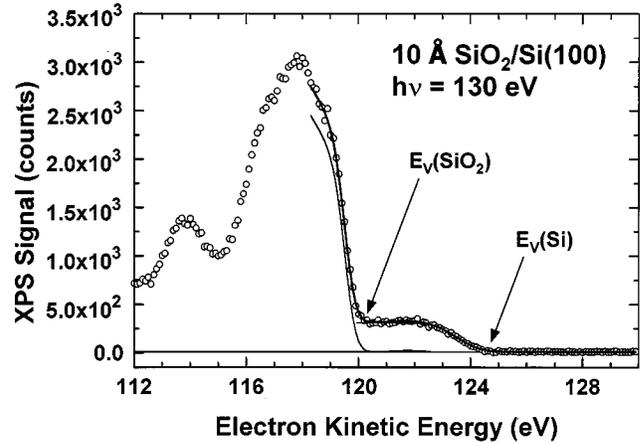


FIG. 3. Closeup view of the silicon and silicon dioxide valence-band edges measured for a 10 Å SiO₂ film grown on Si(100) substrate using a photon energy of 130 eV. The fitting functions are described in the text.

Fits such as these, made using samples of similar thickness and various postoxidation anneal temperatures, were used to derive an average value for ΔE_V of the thin SiO₂/Si(111) interface of 4.54 ± 0.06 eV. ΔE_V was found to be quite constant independent of annealing. Similarly, we have fit the valence-band edge spectra for thin SiO₂ films on the Si(100) substrate. These spectra are similar (see Fig. 3), but with two distinct differences (i) the parabolic peak is much less for the Si substrate, and (ii) onset for Si bulk is much broader, at nearly twice the width of the peaks encountered so far (~1.5 eV compared to 0.7 eV). Again, the ΔE_V values obtained appear independent of annealing treatment, but show a distinct substrate-orientation dependence as pointed out by Alay and co-workers.¹² For ~10 Å SiO₂/Si(100) we find $\Delta E_V = 4.35 \pm 0.06$ eV, which is 0.19 ± 0.08 eV lower than for Si(111). Quantitatively these results compare favorably with previous work (see Table I). However, the present work is done with better resolution and device-proven processes, so we believe our work to be superior.

This direct measure of the valence-band offset can be compared with an indirect approach as well.¹³ In particular, this ΔE_V value can be used in conjunction with $(E_V - E_{CL})$ values (the electron energy difference between Si(2p) core level peak and valence band edge) measured for thin and thick SiO₂ films, in order to derive a Si-SiO₂ core level shift comparable to known values.^{1,2,11} The estimated ΔE_{CL} value is given by:

TABLE I. Compared band offset measurements (values are given in eV).

Value	Si(100)	Si(111)	$\Delta\text{Si(100)-Si(111)}$
ΔE_V (eV)	4.3 ^a	4.5 ^b	
	4.43 wet ^c	4.36 (dry) ^c	0.13 ^c
	4.49 dry ^c		
	4.54 ± 0.06 eV ^d	4.35 ± 0.06 ^d	0.19 ± 0.08 ^d

^aReference 2.

^bReference 1.

^cReference 12.

^dPresent work.

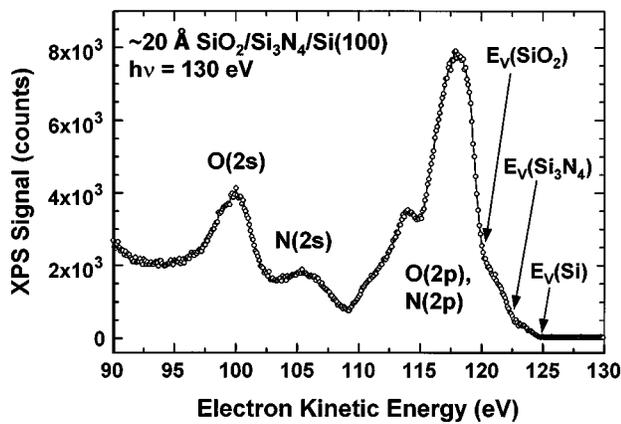


FIG. 4. Valence-band scan measured at 130 eV photon energy for a ~ 20 Å Si₃N₄ film deposited on Si(100) using the RPECVD method. A silicon dioxide overlayer resulting from atmospheric exposure is the dominant feature. In addition, the Si₃N₄ valence-band edge appears between those of silicon substrate and SiO₂. The N(2s) peak at ~ 106 eV kinetic energy is evident, and resembles the O(2s) peak at ~ 100 eV.

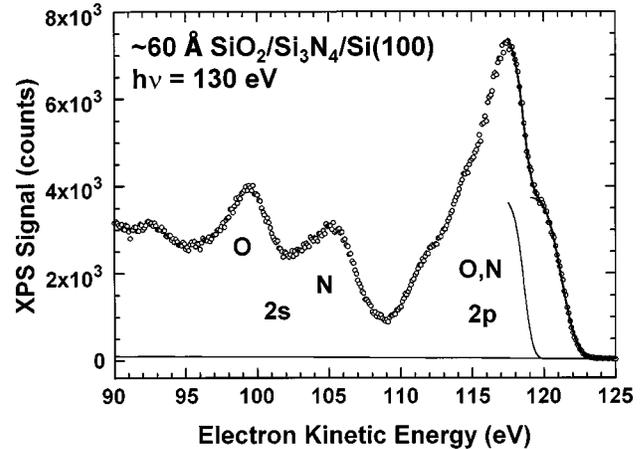


FIG. 5. Valence-band scan measured at 130 eV photon energy for a ~ 60 Å Si₃N₄ film deposited on Si(100) using the RPECVD method. This film is quite thick compared to the electron escape depth (~ 5 – 10 Å) so that no substrate signal is seen. The large valence-band offset for SiO₂/Si₃N₄ measured from this spectrum differs from that measured for thinner films, in part due to photoelectron hole screening by silicon substrate.

$$\Delta E_{CL} = \Delta E_V(\text{Si/SiO}_2) + (E_V - E_{CL})(\text{SiO}_2) - (E_V - E_{CL})(\text{Si}). \quad (2)$$

We can average the Si(111) and Si(100) results for ΔE_V to give 4.44 eV, and obtain an average value of $(E_V - E_{CL})(\text{Si})$ of 98.52 eV by using data for the same thin (~ 10 Å) SiO₂ film samples. For the $(E_V - E_{CL})(\text{SiO}_2)$ value we turn to a thick film of SiO₂ (~ 80 Å) which yields 98.45 eV. The derived ΔE_{CL} value of 4.37 eV compares very well with a ΔE_{CL} value of 4.36 eV estimated for a 80 Å film using the core-hole screening approach.¹¹

B. Valence-band offsets for thin Si₃N₄ films

We have also measured valence-band offsets for silicon nitride films deposited on Si(111) and Si(100) substrates. An example of such valence-band data for < 20 Å Si₃N₄ films on Si(100) is shown in Fig. 4. The hydrogen-rich silicon nitride (made by RPECVD, using N₂^{*} and SiH₄) is known to react readily with atmospheric water to produce a surface layer of silicon (di) oxide. Thus, the spectra show three distinct offsets: (i) Si substrate, (ii) Si₃N₄, and (iii) SiO₂. We have used these data to measure ΔE_V for the Si₃N₄/Si interface. Unfortunately, the overlapping spectra in this case makes the Si₃N₄/Si offset ΔE_V less clear. In addition, the Si₃N₄ onset was not sharp enough to measure for many films thinner than ~ 16 Å. From the best of such data, we arrive at an average value for ΔE_V (Si₃N₄/Si) of 1.78 ± 0.09 eV for an average total film thickness (oxide and nitride) of 18 ± 3 Å. We could not find any statistically significant differences between samples of difference substrate orientation or annealing treatment.

We can estimate the Si₃N₄/SiO₂ valence-band offset from these data as well. Again, using a pair of broadened step functions, we have fit the nitride and oxide onsets from the spectra and found an average Si₃N₄/SiO₂ valence-band offset of 2.66 ± 0.14 eV. It is comforting to find that the ΔE_V

values measured independently for Si–SiO₂, Si–Si₃N₄, and SiO₂–Si₃N₄ follow a simple additivity rule: i.e., $\Delta E_V(\text{Si–SiO}_2) = \Delta E_V(\text{Si–Si}_3\text{N}_4) + \Delta E_V(\text{Si}_3\text{N}_4\text{–SiO}_2)$. In this case, adding the two nitride-relative offsets 2.66 and 1.78 eV yields 4.44 eV which is precisely the average of the ΔE_V values for the SiO₂ films on the two crystal faces (4.45 ± 0.09 eV). However, when we measure the SiO₂–Si₃N₄ ΔE_V value from spectra of thicker films (~ 60 Å), we find it much higher (see Fig. 5). The ΔE_V value of 3.06 eV measured from the spectra in this figure may be higher due to the screening effect difference for different oxide overlayer thickness, as discussed below.

IV. DISCUSSION AND CONCLUSIONS

The valence-band offsets for silicon/silicon oxide and silicon/silicon nitride have been measured with good accuracy using soft x-ray photoemission. These values are critical in the design of oxide-semiconductor devices. In agreement with previous workers, we have found a difference in valence-band offset between the Si(100) and Si(111) crystal interfaces with silicon dioxide. This can be correlated with the number and type of other species at the interface, such as dangling bond defects or hydrogen.¹⁴ This interpretation would suggest that the Si(111) interfaces have less interface H, assuming no dangling bonds. A second explanation for the ΔE_V difference is the orientation of the interface bond dipoles relative to the surface normal. The interface bond dipole is more aligned with the surface normal for the (111) orientation and less aligned (more glancing) for the (100) orientation. If the contribution of the interface bond dipole to the valence-band offset (total interface dipole) follows a cosine rule, this would also explain the lower ΔE_V for Si(100)/SiO₂ relative to Si(111)/SiO₂.

The silicon nitride valence-band edge has also been measured relative to those of Si bulk and SiO₂. These values appear to be less sensitive to the underlying Si crystal orien-

tation. The Si₃N₄-SiO₂ ΔE_V has been found to be somewhat film thickness dependent, increasing by ~ 0.4 eV between 18 and 60 Å film thicknesses. This can be explained as a result of core-hole screening by image charge in the higher k silicon substrate. In other words, the high dielectric constant ϵ_{opt} mismatch ($\Delta\epsilon_{\text{opt}} = 12 - 2 = 10$) between silicon and the SiO₂ substrate is likely to be responsible for this shift. The mismatch is about half as great in the case of screening by the Si substrate of silicon nitride ($\Delta\epsilon_{\text{opt}} = 12 - 7 = 5$). This screening effect causes lower binding energies for thin films and higher binding energies in thicker films.

The results presented here can be used to derive values for the conduction-band offsets as well, using the known E_g values. For example, the known SiO₂ gap energy of 8.95 eV¹⁵ implies a Si-SiO₂ ΔE_C of 3.38 eV (using the average ΔE_V of 4.44 eV and Si bandgap of 1.1 eV).

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