Comparison of ultrathin SiO$_2$/Si(100) and SiO$_2$/Si(111) interfaces from soft x-ray photoelectron spectroscopy

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The limitations of soft x-ray photoelectron spectroscopy (SXPS) for determining structural information of the SiO$_2$/Si interface for device-grade ultrathin (~6–22 Å) films of SiO$_2$ prepared from crystalline silicon by remote plasma assisted oxidation are explored. The main focus of this article is the limitation of data analysis and sensitivity to structural parameters. In particular, annealing data shows a significant decrease in the integrated density of suboxide bonding arrangements as determined from analysis of SXPS data. These decreases and changes are interpreted as evidence for reorganization of specific interface bonding arrangements due to the annealing process. Moreover, these results suggest that sample preparation and processing history are both critical for defining the nature of the SiO$_2$/Si interface, and therefore its electrical properties. Quantitative estimates of the interface state densities are derived from SXPS data revealing ~2 monolayers (ML) of suboxide as prepared and ~1.5 ML of suboxide after rapid thermal annealing at 900 °C for both Si(100) and Si(111) substrates. Comparison of the individual suboxide bonding state densities indicate for both Si substrate crystallographic orientations that annealing causes a self-organization of the suboxide consistent with bond constraint theory. © 2006 American Vacuum Society. [DOI: 10.1116/1.2218865]

I. INTRODUCTION

It has been established that the SiO$_2$/Si interface in metal-oxide-semiconductor (MOS) devices is not an atomically abrupt interface but consists of ~0.35 nm (or 1–2 monolayers) of silicon suboxide. As silicon-based metal-oxide-semiconductor applications push the scale of discrete components ever smaller, a quantitative understanding of the semiconductor applications also provides a foundation for investigating transitions at abrupt interfaces but consists of

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$I$.

Effect of annealing are reported and compared with the Si(111)/SiO$_2$ interface. Our purpose is to present a more detailed study than previous reports and to compare and define these two interfaces in order to clarify the role of interfacial suboxide bonding states for the technologically important Si(100)/SiO$_2$ interface. Figure 1 shows the raw Si 2p soft x-ray photoelectron spectroscopy (SXPS) data for less than 10 Å of SiO$_2$ on Si(111) in the upper panel (a) and in panel (b) shows the spin-orbit stripped data showing only the Si 2p$_{3/2}$ component. The 0.602 eV spin-orbit splitting of the substrate 2p$_{3/2}$ core level is clearly seen in the raw data and illustrates the typical resolution of ~0.1 eV for the SXPS instrumentation. Three interface peaks are also clearly distinguishable. The precise interpretation of the interface peaks has not yet come to full agreement and at least two separate models are in contention at this time. However, there is general agreement that these interface features arise from suboxide states localized in an interfacial transition region between the noncrystalline stoichiometric silicon dioxide and the crystalline silicon substrate. In this article we follow the previous convention of Keister et al. of labeling these features in SXPS by $I_1$, $I_2$, and $I_3$; these same features have been commonly labeled in the literature by the formal oxidation-state notation as $Si^{1+}$, $Si^{2+}$, and $Si^{3+}$. In photoelectron spectroscopy studies, the $Si^{1+}$, $Si^{2+}$, and $Si^{3+}$ assignment
implies a configuration that corresponds to one, two, and
three O–Si bonding sites at the interface. Our data are con-
istent with this interpretation but we do not claim that all
interface state SXPS data can be correctly interpreted in this
way.

A variety of previous studies have been conducted on
SiO$_2$/Si interfaces using various experimental and theoreti-
cal techniques including photoelectron spectroscopy,\textsuperscript{1,8–17} in-
frared spectroscopy,\textsuperscript{8} density functional calcu-
lations,\textsuperscript{19,20} and scanning tunneling microscopy.\textsuperscript{21} The distribution of in-
terfacial suboxide bonding states varied among these studies
yet with all having very nearly the same amount overall; that
is, an effective thickness of $\sim$0.35 nm. These studies in-
cluded thermal oxidation in various environments (O$_2$, N$_2$O, H$_2$O), thermal oxidation with excited oxygen, dry
O$_2$ oxidation, \textit{in vacuo} oxidation, and electron stimulated
oxidation. Films were formed at various temperatures rang-
ing from 600 to 1100 °C with the exception of the electron
stimulated oxidation being conducted at room temperature.
The $I_2$:$I_1$ ratio in most, but not all, of these previous studies
was roughly similar to the results presented in this study
whereas the $I_3$:$I_1$ ratio is generally significantly larger than
the results presented in this study. Though the effects of an-
nalizing may be trivial for high temperature oxidation, in the
study reported here, the effect of annealing is more important
since the deposition process is a relatively low temperature
process (300 °C). The $I_3$ suboxide peak intensity for the
Si(100) interface is unaffected by annealing and is only
slightly increased for the Si(111) interface. The $I_1$ and $I_2$
suboxide peak intensities, however, change significantly with
annealing. The differences in the interface suboxide bonding
state distributions among the various deposition methods and
studies illustrates that the interface bonding configuration is
sensitive to processing conditions; the initial oxidation pro-
cess and temperature, as well as the post oxidation/
deposition annealing temperature and ambient.

Previously, it has been determined that the relative intens-
ities of the specific interfacial suboxide peaks depend not
only on the oxide and interface quality, but also on char-
acteristics such as annealing temperature,\textsuperscript{1} oxide composi-
tion,\textsuperscript{9} crystal orientation,\textsuperscript{10} nitridation level,\textsuperscript{1} and vicinal cut.\textsuperscript{22,23} The focus of this article is not a survey and comparison of
the SiO$_2$/Si interfaces from various studies but on an analysis
of the effect of annealing on SiO$_2$/Si interfaces formed
on Si(100) and Si(111) substrates by a low temperature oxida-
tion process. In this study, approximately 2 monolayers
(ML) of suboxide form between the oxide and substrate dur-
ing low temperature ($\sim$300 °C) oxidation. Additional post-
growth rapid thermal annealing at 900 °C reduces this to
roughly 1.5 ML. A comparison of the relative suboxide bonding
state densities indicates a reorganization of the in-
terface upon annealing consistent with bond constraint
theory.\textsuperscript{24} The currently accepted model of the device-quality
SiO$_2$/Si interface includes a defective silicon layer and an
$\sim$0.25–0.35 nm interfacial transition region of silicon
suboxide.\textsuperscript{24} The new study for the SiO$_2$/Si(100) interface
reported herein gives further evidence for the small but finite
size of the interfacial transition region and the distribution of
suboxide bonding state densities within this region.

II. EXPERIMENTAL DETAILS

Ultrathin films of SiO$_2$ were formed by remote plasma
assisted oxidation (RPAO) of Si(100) and Si(111) substrates
after removal of native oxide by standard wet chemical pro-
cedures. Native oxide was removed from Si(100) substrates
by 1:50 HF and from Si(111) substrates by 40% NH$_4$F. Sub-
strates were subsequently rinsed in de-ionized water, blown
dry with dry N$_2$ and immediately loaded into the oxidation
system. The substrates were exposed to plasma-excited oxy-
gen at a substrate temperature of 300 °C. Oxygen and he-
ilium flowed through the oxidation chamber at 20 and
200 SCCM (standard cubic centimeters per minute) respect-
ively while maintaining a chamber pressure of 0.3 Torr. The
plasma excitation region was isolated from the chamber in
which the oxidation took place, and this process has been
referred to in Ref. 24 as a RPAO process. The oxygen was
excited using a 13.56 MHz rf plasma source at 30 W of
power. This procedure has been shown to produce low defect
density Si–SiO$_2$ interfaces as revealed by electrical studies
of metal oxide semiconductor capacitors (MOSCAPs) and
metal oxide semiconductor field effect transistors (MOSFETs),
if followed by a deposition of SiO$_2$ or a Si oxynitride alloy by remote plasma enhanced chemical vapor
deposition (RPECVD) and a thermal anneal at 900 °C.\textsuperscript{25–27}
The oxidation rate of the silicon substrate, determined using
\textit{in situ} Auger electron spectroscopy (AES) is \( I_{ox} \sim 7 \times 10^{10} \),
III. RESULTS

Figure 2 compares typical Si 2p\(_{3/2}\) spectra for ~10 Å SiO\(_2\) films oxidized from Si(100) and Si(111). The data are normalized to the substrate height and the binding energy is given relative to the substrate peak position. An empirical background has been subtracted from the spectra. The Si 2p\(_{3/2}\) component was mathematically stripped to clearly identify the discrete suboxide peaks. The binding energy of the Si-ID (substrate) peak was measured to be ~99.4 eV with respect to the Fermi level of the analyzer. The SiO\(_2\) peak has a relative binding energy of ~3.8 eV. The suboxides I\(_1\), I\(_2\) and I\(_3\) have relative binding energies of ~0.9, ~1.8, and ~2.5 eV, respectively. The most notable difference between the spectra is that the I\(_1\) peak intensity is larger for SiO\(_2\)/Si(111) compared to SiO\(_2\)/Si(100) while the I\(_2\) intensity is significantly reduced. This is expected based on the crystal structure of the two silicon faces. The Si(111) crystal face has single Si dangling bonds and the I\(_3\) suboxide is native to that face whereas the Si(100) crystal face consists of silicon dimers that naturally result in I\(_3\) suboxide.

Rapid thermal annealing of the SiO\(_2\)/Si films significantly changed the interface suboxide bonding state intensities. This is readily seen in Figs. 3 and 4 which compare the suboxide region of the Si 2p\(_{3/2}\) spectra of the as oxidized samples with samples annealed at 900 °C for SiO\(_2\)/Si(100) (Fig. 3) and SiO\(_2\)/Si(111) (Fig. 4). As in Fig. 2, the data are normalized to the substrate peak and the binding energy given relative to the substrate peak. Fitted peaks are shown to emphasize the differences in the spectra. Slight deviations between the data and fitted curve are the result of constraining the fit for quantitative analysis as discussed below and displaying peaks fitted using the raw Si 2p data with mathematically spin-orbit stripped data. Upon annealing, the I\(_1\) and I\(_3\) suboxide states of the SiO\(_2\)/Si(100) film decrease slightly, indicating a slight phase decomposition into Si- and/or O-rich phases. For the SiO\(_2\)/Si(111) film, annealing causes a dramatic reduction of the I\(_2\) peak intensity. This indicates not only phase decomposition, but also a change in the structure of the interface.

To conduct a quantitative analysis of the interfaces, the full Si 2p spectra were modeled using five pairs of spin-orbit split Voigt functions optimized with a nonlinear least-squares fit to the raw data. The background was empirically modeled with four parameters \((a+bx+c\lambda^d)\). Each spin-orbit split peak pair had a common Gaussian width and the Lorentzian width...
was common to all peaks. The following procedure was used to prevent ambiguous fitting due to the large number of parameters. The Lorentzian width (80 meV), spin-orbit splitting (0.602 eV), and branching ratio (0.5) were chosen and fixed. Spectra were initially fit with these constraints and the Gaussian width for each peak at each photon energy was averaged. These averages were then used as further constraints for final fits. The positions and heights of the suboxide bonding states were chosen and averaged. These averages were then used as further constraints for final fits. The positions and heights of the suboxide bonding states were chosen and averaged. These averages were then used as further constraints for final fits.

Utilizing estimates of the escape depth and relative photoemission cross sections, (two dimensional) interface suboxide densities, ISD, were calculated from the SXPS data by considering the ratio of the interface suboxide state peak intensity, Ij, to the substrate peak intensity, I0:

\[
\text{ISD}_j = \frac{I_j \sigma_{\text{Si}}}{I_0 \sigma_j n_{\text{Si}}} \lambda_{\text{Si}}.
\]

where \(\sigma_{\text{Si}}\) is the Si 2p photoemission cross section of the substrate at a given photon energy, \(\sigma_j\) is the Si 2p photoemission cross section of suboxide state \(j\), \(n_{\text{Si}}\) is the bulk (three dimensional) silicon crystal density, and \(\lambda_{\text{Si}}\) is the electron escape depth (at a specific photon energy) in the silicon substrate. The escape depth and ratio of substrate to suboxide cross sections for photon energies of 130, 150, and 200 eV are used from Ref. 10. These data were provided in Ref. 1 and repeated here in Table II. It is instructional to convert these interface state bonding densities into monolayer coverage by normalizing them to the silicon atom density of the particular crystal face (\(n_{111} = 6.78 \times 10^{14} \text{ cm}^{-2}\)).

Table III lists the average interfacial suboxide bonding state densities. The individual and total interface state densities are shown in Figs. 5 and 6 as a function of the annealing temperature. The general trend follows the expectation of the visual comparisons in Figs. 3 and 4. For SiO2/Si(100), the interface states \(I_1\) and \(I_2\) decrease with annealing and for SiO2/Si(111), \(I_2\) decreases dramatically with annealing. For both crystal orientations, the total “thickness” of the interface is \(~2.0\) ML before annealing and \(~1.5\) ML after annealing to 900 °C. After annealing, the ratio of \(I_1:I_2:I_3\) for SiO2

\[
\begin{array}{cccccc}
\text{h\nu (eV)} & \lambda_{\text{Si}} (\text{Å}) & \alpha_{\text{Si}}/\alpha_1 & \alpha_{\text{Si}}/\alpha_2 & \alpha_{\text{Si}}/\alpha_3 \\
130 & 3.3^a & 1.0^a & 0.91^a & 0.59^a \\
150 & 4.8 & 1.0 & 1.0 & 0.68 \\
200 & 6.3 & 1.0 & 1.0 & 0.77 \\
\end{array}
\]

From Ref. 10.

Table I. Representative relative binding energies and peak widths (Gaussian). Data shown for \(h\nu=130\) eV.

\[
\begin{array}{llll}
\text{State (i)} & \Delta BE (\text{eV}) & \text{FWHM (eV)} \\
\text{SiO}_2/\text{Si}(100): & & & \\
\text{Sub} & (0) & 0.37 \\
I_1 & 0.94 & 0.50 \\
I_2 & 1.81 & 0.59 \\
I_3 & 2.50 & 0.57 \\
\text{SiO}_2 & -3.9 & -1.16 \\
\text{SiO}_2/\text{Si}(111): & & & \\
\text{Sub} & (0) & 0.36 \\
I_1 & 0.96 & 0.44 \\
I_2 & 1.48 & 0.58 \\
I_3 & 2.50 & 0.66 \\
\text{SiO}_2 & -4.0 & -1.15 \\
\end{array}
\]

Table II. Parameters used to calculate the interface suboxide state densities.

Table III. Summary of interface suboxide state densities.
oxidized from Si(100) is 1:1:1 and for SiO₂ oxidized from Si(111) is 3:1:2.

IV. DISCUSSION

Drawing upon a host of investigations of the SiO₂/Si interface including medium energy ion scattering, spectroscopic ellipsometry, cathodoluminescence, and SXPS, Lukovsky and Phillips reviewed the SiO₂/Si interface, focusing on Si(111). They concluded that annealing causes decomposition of interfacial suboxide into Si-rich and O-rich composition regions and a reorganization of the interface to form a strain relaxation region between the SiO₂ and substrate. This conclusion was based on an extension of the bond constraint theory originally applied to chalcogenide glass.

Upon oxidation, the distribution of suboxides is kinetically prevented from forming the energetically favored arrangement. Annealing at 900 °C allows a rearrangement of the SiO₂/Si interfacial suboxide bonding to form ~1 ML of suboxide (0.3 nm) which provides a strain relief mechanism between the SiO₂ and Si. Interpreting the interface suboxide bonding states as quantitatively representing the formal oxidation state of the silicon atoms, this study demonstrates that both the SiO₂/Si(100) and SiO₂/Si(111) interfaces are consistent with the interpretation given in that review. For the purpose of this discussion, the assumption is made that the I₁, I₂, and I₃ peaks represent Si atoms with one (Si¹⁺), two (Si²⁺), and three (Si³⁺) bonds to oxygen atoms in the interface.

Hinds et al. established that bulk SiO decomposes into Si and SiO₂ upon annealing. This is a kinetically limited reaction; there are no stable SiO phases to block the decomposition. The results presented here indicate similar phase decomposition in the SiO₂/Si interface. Because a Si atom bound to two two oxygen atoms (SiO) is not native to the SiO₂/Si(111) interface, a qualitative comparison of the two-dimensional (2D) and three-dimensional (3D) decomposition is reasonable. Hinds illustrated that bulk reaction is >90% complete after annealing at 900 °C. This study reveals that at the SiO₂/Si(111) interface, the I₂ peak intensity (representing the Si²⁺ density) is reduced by ~60% after annealing at 900 °C. Further decomposition is presumably prevented by the crystalline silicon to amorphous oxide bonding transition.

The relative interface suboxide state densities before and after annealing are revealing. A random Si¹⁺: Si²⁺: Si³⁺ bonding distribution between tetravalent Si and O is 4:6:4. The RPAO of silicon is conducted at a relatively low substrate temperature so there is insufficient thermal energy for the bonding arrangement to relax during oxidation. Thus a random bonding arrangement with emphasis on the suboxide “native” to the Si surface is anticipated. The as-oxidized RPAO SiO₂/Si(111) interface has an I₁:I₂:I₃ suboxide bonding distribution of ~9:~6:~4. This is consistent with 0.5 ML of the native Si¹⁺ suboxide with the remaining suboxide randomely distributed. The as oxidized SiO₂/Si(100) interface has an I₁:I₂:I₃ suboxide bonding distribution of ~6:~6:~4. A random distribution with an additional 0.5 ML of the native Si²⁺ would result in an overall distribution of ~4:~11:~4. It is anticipated that this distribution is not achieved because of step edges on the (100) surface. Step edges are abundant on Si(100) substrates and would enhance Si¹⁺ bonding at the expense of Si²⁺ bonding.

Annealing at 900 °C provides sufficient thermal energy for the interface to relax, redistributing the suboxide densities. The distribution is ~1:~1:~1 for the SiO₂/Si(100) interface and ~3:~1:~2 for the SiO₂/Si(111) interface. It has been demonstrated by other studies that after thermal annealing at 900 °C, the Si–SiO₂ transition region includes ~1 ML of suboxide with an average composition of SiO₂. The SXPS data in this study reveal ~1.5 ML of suboxide for both Si(100) and Si(111). A third of this (0.5 ML) is due to the native bonding at the Si surface while the remaining 1.0 ML is a distribution of suboxides with an average composition of SiO (Si²⁺).

An interesting comparison can be made between this study and the study of thermally oxidized Si(100) by Lu.
et al.\textsuperscript{11,12} Lu et al. studied the interface suboxide distribution of the SiO\textsubscript{2}/Si(100) interface for oxides thermally grown between the temperatures of 700 and 1000 °C and for oxides grown at 700 °C and subsequently annealed up to 1000 °C. In both cases, the higher processing temperature, whether during oxidation or during postoxidation annealing, resulted in higher densities of Si\textsuperscript{2+} and Si\textsuperscript{3+} bonding whereas the Si\textsuperscript{1+} bonding was unaffected. A thermodynamically (rather than kinetically) governed strain relief mechanism is postulated as the basis for this change. In this study, the \(I_1\) and \(I_2\) (or Si\textsuperscript{1+} and Si\textsuperscript{2+}) suboxides of the as grown SiO\textsubscript{2}/Si(100) sample are \(\sim 1.6\) times larger than the thermally grown oxides of Lu et al. The \(I_3\) (or Si\textsuperscript{3+}) suboxide is roughly the same in both studies. Upon annealing, the \(I_1\) and \(I_2\) suboxides decrease to roughly the same as in thermally grown oxides of Lu et al. This is consistent with an interpretation that the lower temperature of RPAO does not provide sufficient energy to allow significant relaxation during oxidation and that the resulting extra Si\textsuperscript{2+} and Si\textsuperscript{3+} bonding is removed during rapid thermal annealing.

V. CONCLUSIONS

Using high-resolution SXPS investigation of ultrathin SiO\textsubscript{2} films oxidized from Si(100) and Si(111), the evolution of the interface suboxide states of the SiO\textsubscript{2}/Si interface was studied. Provided that the interface suboxide states resolved by SXPS represent formal oxidation states of silicon, the trends shown in Figs. 5 and 6 are indicative of the self-organization model of an amorphous/crystalline interface. As oxidized, the suboxide states tend toward a random distribution that is tailored by the intrinsic suboxide bonding of the Si crystal surface. After annealing at 900 °C, the non-native portion of the suboxide reorganizes to form an average composition of SiO while the suboxide native to the particular Si crystal face remains. This study indicates that the Si–SiO\textsubscript{2} transition region is common to both the Si(100) and Si(111) surfaces and differs only in the intrinsic suboxide bonding at the Si surface. It has also been illustrated that processing conditions play a significant role in defining the bonding character of the interface.


References