XPS study of pulsed Nd:YAG laser oxidized Si

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Abstract

X-ray photoelectron spectra (XPS) of thin SiO 2 layers grown by pulsed Nd:YAG laser at a substrate temperature of 748 K are presented. The peak decomposition technique combined with depth profiling is employed to identify the composition and chemical states of the film structure. It is established that the oxide is non-stoichiometric, and contains all oxidation states of Si in different amounts throughout the film. The interface Si/laser-grown oxide is not abrupt, and the coexistence of Si 2O 3 and Si 2O suboxides in a relatively wide interfacial region is found. It is concluded that post-oxidation annealing is necessary in order to improve the microstructure of both oxide and near interface region.

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1. Introduction

The great success of microelectronics, during the past several decades is related with the fact that Si has native oxide that is SiO 2 – nearly ideal insulator giving practically perfect interface with Si. The continual scaling of CMOS technologies, however, has pushed the Si/SiO 2 system to its very physical limits and the development of future generations (Gigabit scale) of both Dynamic Random Access Memories (DRAMs) and MOSFETs require alternative dielectric films with a high dielectric constant, (high-k) [1–3]. At the same time, new methods of oxidation of Si for extremely thin SiO 2 growth is still a subject of ongoing investigations [4–8]. These methods are in fact new trends in the efforts to obtain dielectric (mainly SiO 2-based) layers with enhanced capacitance properties to meet the requirements of the high density DRAMs. Among them, the techniques enabling local and low temperature oxidation are of a special interest. For example, the local oxidation by Atomic Force Microscopy (AFM) has received much attention [5,6]. At present, however, AFM-grown SiO 2 shows very poor dielectric quality compared to thermally grown SiO 2 [6] and is not suitable as an active dielectric. It is not convenient for mass production either. Despite the fact that the techniques of laser oxidation are far from their full optimization, they have a great potential for future device applications. In addition to the advantages such as local oxidation and low processing temperatures, laser-assisted oxidation provides a good control over the thickness of very thin films including SiO 2 [7,9–12]. Recently, we have reported [7,13] that the amorphous thin SiO 2 films could be successfully obtained by pulsed Nd:YAG laser in O 2 ambient at relatively low temperatures. It was established that an interval of laser beam energy density exists in which the oxidation occurs without surface melting. Electrical data of laser-oxidized SiO 2 layers have shown typical MOS behavior and the laser-grown
oxide generally has parameters close to those of thermally
grown SiO2 in terms of interfacial defect charges, slow state
densities and leakage current levels. The results implied,
however, that the oxide through the depth is most likely
non-stoichiometric, with excess Si. It was speculated that
the structural non-perfections are responsible for the
detected high density of oxide charge. Obviously, the pre-
cise structural analyses are required for laser-oxidized
films. It is known that X-ray Photoelectron Spectroscopy
(XPS) could be successfully used to detect as well as to
identify various suboxides and their distribution in the oxide
and at the interface. In this article, XPS investigation
of laser-oxidized SiO2 is reported. The best oxidation con-
ditions in terms of laser beam energy density and substrate
temperature are used as determined by the capacitance–
voltage and current–voltage characteristics [7]. Layers with
thickness \( d \) of 40 nm were studied.

2. Experimental procedure

Chemically cleaned p-type (100) 15 \( \Omega \cdot \text{cm} \) Si wafers (a
standard 2:1 solution of \( \text{H}_2\text{SO}_4 \) and \( \text{H}_2\text{O}_2 \)) were used as
substrates. After the cleaning (including the final step of
dipping into dilute HF to remove the native oxide), the
samples were laser oxidized in vacuum chamber evacuated
to a base pressure below 0.13 Pa. The substrate was heated
to the temperature of 748 K prior to oxidation. \( \text{O}_2 \) gas was
introduced into the chamber (working gas pressure, \( p \), was
123 Pa) after reaching the desired substrate temperature.
Nd:YAG laser at 1064 nm, (EKSPLA Pulsed Laser NL
301) was used to induce oxidation. The laser output is com-
posed of a pulse train with individual pulses typically of
4.7 ns. More details on the laser parameters and the process
of oxidation can be found elsewhere [7]. The approach used
is only briefly described here. A computer controlled \( X-Y \)
scanner system was used to direct the laser beam on a cer-
tain region on the substrate with controllable dimensions.
By means of the scanner system, the laser beam was
scanned over an area of the substrate of approximately
4 \( \times \) 4 mm\(^2\) and it can be further reduced by the software.
The laser beam energy density, \( P \), was 3.4 J/cm\(^2\) per pulse.
The preliminary measurements showed that the small vari-
ations of \( P \), from 3.35 to 3.45 J/cm\(^2\), had no effect on the
XPS data. According to the previous results [7], this value of
\( P \) is close to the laser fluence corresponding to surface
melting but without crossing it. It enables oxidation pro-
cess without surface melting. The oxide thickness and
refractive index of the layers obtained were measured by ellipsometry (\( \lambda = 632.8 \) nm). The refractive index was 1.45.

XPS was used to analyze the composition and chemical
states of laser-oxidized SiO2 film and its interface with Si.
The data were obtained using an Al K\(_\alpha\) (1486.6 eV) excita-
tion source in ESCALAB Mk II apparatus (VG Scientific)
with a residual gas pressure better than 1 \( \times \) 10\(^{-8} \) Pa. All
spectra were taken at 300 K. The photoelectrons were sep-
arated by a semispherical analyzer with a pass energy of
10 eV and an instrumental resolution of 1.0 eV measured
as the Full Width at Half Maximum (FWHM) of the Ag
3d\(_{5/2}\) photoelectron peak. The energy position of the peaks
was determined with an accuracy of 0.1 eV. The photoelec-
tron lines of Si2p and O 1s were recorded. The binding
energies \( E_b \) have been corrected for sample charging effect
with referenced to the C 1s line at 285.0 eV for the surface of
the oxide, and to the Si2p line of the elemental Si at
98.7 eV for all spectra obtained after ion sputtering. The
peak positions and FWHM were determined from least
square fitting using the instrument’s software. The peak
shapes for all peaks were fixed to a mix of Gaussian–
Lorentzian functions. The final fitting was made iteratively.
The composition was calculated using the standard soft-
ware. The spectra were obtained under the angle of 90°,
(with respect to the surface plane) of photoemitted elec-
trons. The chamber was also equipped with an ion source
that is equipped with Ar\(^+\) to determine
the concentration profiles of various species. The argon ion beam was with an energy of 1.5 keV and a cur-
rent density of 12 \( \mu \text{A/cm}^2 \). The angle of incidence of the
sputtering beam was 40° with respect to the surface of
the layer. The experimental curves are as-recorded data
after Shirley background subtraction. It is very important
to minimize the adverse effects of the ion beam on the sam-
ple stoichiometry during the ion sputtering. It is known [14]
that 1–1.5 keV argon ions sputter conventional SiO2 keep-
ing its stoichiometric ratio, i.e., the ions remove Si and O at
a rate very close to 1:2. Therefore, we assume that eventual
unfavorable effects of the ion beam sputtering such as a
preferential sputtering should not influence considerably
the experimental results and conclusions drawn from them.
During sputtering the structure of the SiO2 layer is likely to
be damaged but this is not reflected on the Si2p binding
energy or its line width. For sputtering times, \( t_s \), of 0.5–
140 min, the thickness reduction as measured by XPS [15]
was linear with \( t_s \) and the sputtering rate was obtained to
be 3 Å/min. The sputtering rate determined by the mea-
sured oxide thickness and \( t_s \) was approximately the same,
(2.9 Å/min) indicating that both methods are correct.

3. Results and discussion

3.1. Si2p spectra

Fig. 1 presents the variation of the experimental Si2p
spectra through the depth of the films, \( d_0 \) is the distance
from the surface). The spectrum at the surface reveals a
peak in the C 1s region (not shown in the figure) with neg-
ligible intensity demonstrating that the surface remains
clear enough after short air exposure. The carbon signal
(at 284.6 eV, indicating the presence of C–C bond) is due
to adsorbate which disappears when surface is sputtered
slightly, \( t_s \sim 0.5–1 \) min). Fig. 2(a)–(d) illustrates spectra
for several selected distances from the surface. The solid
line represents as-recorded data. The peak positions
extracted from the depth spectra, FWHM of the peaks
and their shift with respect to the elemental Si line are inserted in the figures. Two symmetrical peaks could be distinguished in the spectrum at the surface: one is located at 103.1 eV, referred as Si$_{\text{oxide}}^{2p}$, (FWHM = 2.1 eV) which is typical position of SiO$_2$ [16–18] and a second lower binding energy line is located at 98.7 eV, (FWHM = 1.4 eV) referred as Si$_{\text{Si}}^{2p}$ and associated with a signal from the substrate. The former one has a higher intensity. The analysis of the evolution of the peaks with $t_s$ shows the following: the Si$_{\text{oxide}}^{2p}$ line shifts to lower energy with increasing the sputtering time, (its position is 102 eV for $d_0 \sim 12$ nm); Si$_{\text{Si}}^{2p}$ line deforms, and Si$_{\text{oxide}}^{2p}$ feature develops to a two-peaks-structure. At a depth of 4.3 nm from the surface, Si$_{\text{oxide}}^{2p}$ is due to the photoelectrons from SiO$_2$, (or Si$^{4+}$ according to the well known classification) and from another phase namely SiO, (or Si$^{2+}$). The intensity of Si$^{2+}$ component is nearly six times smaller than that of the main SiO$_2$ peak. The sum of the three peaks, (elemental Si, (Si$^{0}$), stoichiometric SiO$_2$, (Si$^{4+}$) and intermediate Si$^{2+}$ oxidation state), gives a spectrum equal to the experimental one. The Si$^{4+}$ and Si$^{2+}$ lines present in the spectra up to $d_0 \sim 24$ nm, but their intensities change with $t_s$: when thinning the oxide the intensity of stoichiometric Si$^{4+}$ line decreases monotonously, and the intensity of Si$^{2+}$ one increases up to a constant value in the $d_0$ range of 12–20 nm indicating the enhanced impact of the suboxide in the depth of the layer. The Si$^{2+}$ peak is shifted by 2.1–1.7 eV from that of elemental Si (in dependence on $d_0$) which is consistent with the shift usually observed for this suboxide [17–20]. The qualitative change in the spectra is observed for $d_0$ greater than 20 nm, (Figs. 1 and 2): the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Comparison of Si2p spectra for various distances $d_0$ from the surface.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Decomposition of Si2p spectra for different $d_0$: (a) 0 nm; (b) 4.3 nm; (c) 24 nm; (d) 40 nm; (— as-recorded data, --- decomposition of the components). The corresponding oxidation states are indicated in the figures; $\Delta$ is the energy shift of the various peaks with respect to Si$^{0}$ line.}
\end{figure}
SiO$_2^{\text{oxide}}$ line changes its typical form to a broad peak with reduced intensity. The most pronounced effect of the change, however, is the missing of a SiO$_2$ signal for $d_0 > 24$ nm. The deconvolution of the spectra yields a set of three peaks (Fig. 2(c)) corresponding to Si$^{0}$ and two new intermediate oxidation states of Si: Si$_2$O, (Si$^{1+}$) and Si$_2$O$_3$, (Si$^{3+}$) [18,19]; the Si$^{3+}$ peak disappears. The intensity variation of the different peaks towards the interface with Si is such that after $d_0 \sim 25$ nm, the peak of Si$^{0}$ dominates in the spectrum; the intensity of Si$^{1+}$ weakly increases and Si$^{3+}$ peak gradually loses its potency, but even just at the interface its intensity is not negligible (Fig. 2(d)). The Si$^{1+}$ line is shifted by 1.4–1.5 eV and the Si$^{3+}$ by 3.0–3.4 eV from that of Si$^{0}$, respectively. This is in accordance with the observations [16–20] of oxidation state peak shift of about 1 eV, (with respect to each other) starting from the line of elemental Si. The chemical shift $\Delta$ of Si$^{3+}$ signal is 4.4 eV at the surface and nearly the same value up to $d_0 \sim 11$ nm. This value is larger than that usually obtained (3.8 eV) for thin SiO$_2$ films [21]. Similar values of $\Delta$ have been reported previously [22] and have been associated to structural imperfections and non-homogeneity of the layers. That is why we assigned the detected chemical shift to the presence of structural non-perfections in the laser oxidized films, i.e. strained and/or broken Si–O bonds. The nearly constant value of $\Delta$ for SiO$_2$ signal indicates a uniform distribution of these imperfections in the part of the layer that contains SiO$_2$, i.e., up to $\sim 11$ nm.

Fig. 3 in which the area under the peaks of the four oxidation states of Si as well as the area under the Si$^{0}$ peak is plotted as a function of $d_0$ exhibits the distribution of the observed oxidation states. The film is understoichiometric containing all possible oxidation states and their contributions depend on $d_0$. SiO$_2$ and SiO present up to $d_0 \sim 24$ nm, and SiO$_2$ dominates in a surface sublayer with a thickness of about 15 nm; Si$_2$O and Si$_2$O$_3$ suboxides present in the whole region extending from the very interface up to 15–16 nm inwards the oxide where the prevalent oxidation state is Si$_2$O. The quantity of each of the suboxides is constant in the near interfacial region ($\sim 8$ nm from the interface); the concentration of Si$_2$O$_3$ is threefold smaller. The coexistence of these intermediate oxidation states in the interfacial region indicates a strong deviation from the ideal atomically abrupt interface. There exists excess Si in a wide interfacial transition region. If we assume that the interface with Si is defined by the ellipsometrically measured thickness of the oxide, the full width of the interfacial region is approximately 15 nm; it starts at $d_0 \sim 25$ nm and extends to the very interface where a strong increase of the elemental Si intensity is observed due to the intensification of the signal from the substrate. As is seen from Figs. 2 and 3, however, Si$^{0}$ line is in fact detected in the whole oxide layer even at the surface. It stands to a reason to interpret this peak in the depth spectra up to $d_0 \sim 25$ nm with the presence of non-oxidized Si. An alternative explanation could also be the effect of the thickness non-uniformity of the laser oxidized films, detected previously [7] in a range around beam center. The thickness profile was fitted to a Gaussian curve and the flat range (active oxidized spot on the wafer) as about 1 mm from the center across which the thickness variation is within 10%. Thus, the thickness non-uniformity could be responsible for the significant intensity of the elemental Si. A nearly constant intensity of Si$^{0}$ for $d_0 \leq 25$ nm is a support of this assumption. On the other hand, the presence of pinholes in the film cannot also be a priori ruled out. Films with pinholes usually exhibit a larger signal from the bulk Si, and this is exactly what we see here. If the layer is not continuous, it will give rise to an extra emission from pure Si through pinholes. In fact, no preference to any of these possible interpretations of Si$^{0}$ signal, observed in the oxide up to $\sim 25$ nm, can be given at present. However, considering the electrical and optical properties of laser-oxidized SiO$_2$ [7,13], we speculate that both the thickness non-homogeneity and the presence of pinholes are the most possible reasons for the observed behavior of Si$^{0}$ signal.

3.2. O 1s spectra

The O 1s spectrum at the surface of the sample can actually be fitted to two Gaussian components, (Fig. 4(a)). The main peak located at 532.3 eV, FWHM = 1.8 eV is close to the expected position of SiO$_2$ [23] but with an indication of the influence of a lower oxidation state. The line at 530.1 eV, FWHM = 1.4 eV with $\sim 3.5$ times smaller amplitude can be associated with poor oxidation state combined with surface contamination, such as carbon oxide or hydroxide. Furthermore, according to the fitting, the energy positions of these peaks are not practically changed (Fig. 4(b)–(d)). The sum of these lines, however, (i.e., the experimental O 1s peak) changes both its position and shape through the depth of the layer. Fig. 5 shows the evolution of the O 1s spectrum with thinning the film by sputtering; O 1s peak shifts to lower energy for $d_0$ in the range of 11–25 nm, indicating certain structural and compositional changes in the film at these depths, namely enhanced
The effect of suboxides. Subsequently, the binding energy of O 1s line is not changed up to the interface with Si. The evolution of the intensity of two peaks forming O 1s line versus $d_0$ is illustrated in the inset of Fig. 5. The line at 531.1 eV is assigned to the elemental oxygen [23] and we will refer as $O_1$. The higher binding energy line, referred as $O_{1s}$, dominates in the spectra up to $d_0 = 20–22$ nm, (Fig. 4) where its intensity equals to the intensity of the peak of elemental oxygen. The progressive reduction of the intensity of $O_{1s}$ peak as the film is sputtered is detected, while the intensity of $O_1$ one does not change significantly suggesting the presence of elemental oxygen through the whole layer. At present we have no clear explanation for the presence of non-bridging oxygen in the laser-oxidized film. Generally there are two hypotheses for this phenomenon: (i) spontaneous decomposition of some quantity of suboxides during Ar$^+$ bombardment. The low energy of Ar$^+$ ions, (1.5 keV) enables sputtering of SiO$_2$ unambiguously in a stoichiometric ratio, but this energy could be high enough to decompose intermediate oxidation states especially at the places with a large amount of non-perfect bonds (dangling and/or strained bonds) as it emerged indeed in our case. On the other hand, the thickness of the surface damaged layer with altered composition as a result of action of 1.5 keV Ar$^+$ ions is much smaller than the information depth of take off angle used [24]. This means that the XPS signal results from the steady state region of the layer and not from the surface distorted layer. The clarification of these effects is a non-trivial task especially in such kind of non-perfect oxide which is obviously laser-oxidized SiO$_2$ and requires an additional precise investigation. (ii) Various structural non-perfections in

![Fig. 4. O 1s spectra for different $d_0$: (a) 0 nm, (at the surface of the layer); (b) 4.3 nm; (c) 24 nm; (d) 40 nm; (— as-recorded data, --- after deconvolution).](image)

![Fig. 5. Comparison of O 1s spectra for various distances from the surface. Inset shows the depth profiles of $O_1$ and $O_1$ peak intensities.](image)
the layer including topological features and small thickness non-uniformity may introduce an additional charge shift (regardless that the peak positions in the spectra are obtained after removal of charge shift) giving an inaccurate binding energy of the XPS lines. Based on the data, however, it is not possible to accept or to reject any of these two assumptions completely.

4. Conclusion

The XPS data presented here correspond to the pulsed Nd:YAG laser oxidation of Si with a laser beam energy density close to the surface melting but without crossing it. The results imply that the laser assisted growth of SiO₂ is a promising way for obtaining of a nearly stoichiometric SiO₂ in the form of small spots with desirable thickness at low temperatures, (40 nm oxide obtained at 748 K was studied here). The composition of the oxide, however, is not uniform on the entire thickness of the layer. All possible Si oxidation states present in the film in different amount through the depth. The layer contains a dominant SiO₂ and smaller quantity of SiO in the upper half, while Si₂O₃ and Si₂O dominate completely in the wide interfacial region at Si. We speculate that the inevitable thickness non-uniformity of the layers and the eventual presence of pinholes both give rise to substantial emission and are to a great extent responsible to the behavior of Si2p depth profiles. It is noticeable that the laser oxidation produces films with non-perfect and non-abrupt interface with Si composed of lower oxidation states (excess Si). In this scheme, one can conclude that the subsequent annealing process is absolutely needed for pulsed laser-oxidized SiO₂ layer to reduce the contribution of Si suboxides and bond-related imperfections to a tolerable level as well as to make the interface abrupt enough for device applications.

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