Electrical characterization of thin nanoscale SiO\textsubscript{x} layers grown on plasma hydrogenated silicon

E Halova\textsuperscript{1}, N Kojunharaova\textsuperscript{1,3}, S Alexandrova\textsuperscript{1} and A Szekeres\textsuperscript{2}

\textsuperscript{1}Department of Applied Physics, Technical University of Sofia, 8 Kl. Ohridski Blvd., 1797 Sofia, Bulgaria
\textsuperscript{2}G. Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria

E-mail: nkojuharova@tu-sofia.bg

Abstract. We analyzed the electrical characteristics of MOS structures with a SiO\textsubscript{x} layer grown on Si treated in plasma without heating. The hysteresis effect observed indicates the presence of traps spatially distributed into the oxide near the interface. The shift and the shape of the curves reveal a small oxide charge and low leakage currents, i.e. a high-quality dielectric layer. The generalized \textit{C-V} curve was generated by applying the two-frequency methods on the \textit{C-V} and \textit{G-V} characteristics at frequencies in the range from 1 kHz to 300 kHz and by accounting for the series resistance and the leakage through the oxide layer. The energy spectra of the interface traps were calculated by comparing the experimental and the ideal theoretical \textit{C-V} curves. The spectra showed the presence of interface traps with localized energy levels in the Si bandgap. These conclusions correlate well with the results on this oxide’s mechanical stress level, composition and Si-O ring structure, as well as on the interfacial region composition, obtained by our previous detailed multi-angle spectral ellipsometric studies. The ellipsometric data and the capacitance in strong accumulation of the \textit{C-V} curves were used to calculate the thickness and the dielectric constants of the oxide layers.

1. Introduction

SiO\textsubscript{2} nanostructures exhibit excellent characteristics, such as electrical insulation and visible light transmission, making them promising for applications in optics (photoluminescence, optical isolation, optical waveguides), photochemistry, biomedicine [1], [2]. In general, low-dimensional nanostructured materials have recently attracted considerable attention due to their unique physical, chemical, optical, electrical, magnetic and photocatalytic properties, to name but a few [3].

The modern semiconductor nano- and microelectronics is still largely dominated by the silicon technology. Structures such as Si/SiO\textsubscript{2} have found applications in solar cells, graphite films and carbon nanotubes, new 2D geometries, double gate devices, ballistic nanotube transistors, etc. A detailed discussion of the future development of nano devices can be found in the recent reviews [4-6]. One can conclude that at least in the next decade Si/SiO\textsubscript{2} will remain an important building block in many applications.

\textsuperscript{3} To whom any correspondence should be addressed.
Thermal oxidation at lower temperatures reduces the film's growth rate and quality. The Si interface is of lower quality, higher gate leakage and interface trap density. One method of improvement is the incorporation of hydrogen, which has been widely used in the past decade due to different beneficial effects, such as stabilization of the device characteristics through gettering of impurities and saturation of defects. Hydrogenation is expected to attract further interest in future nanoelectronic applications, as exfoliation of silicon in smart cut process, increasing the carriers’ lifetime in solar cells, etc. Applied to silicon oxide layers on a nanometric scale, hydrogenation can have a beneficial impact by improving the defect and leakage characteristics. Technologically, Si processing, especially pre-oxidation cleaning of the silicon surface, can play a decisive role in growing high-quality thin SiO$_2$ layers at lower oxidation temperatures.

The aim of the present paper is electrical characterization of the interface (111) n-Si/SiO$_x$ formed on Si wafers by exposure to RF hydrogen plasma prior to oxidation. The interface traps density spectra are expected to depend on the amount of incorporated hydrogen. For this purpose, Si/SiO$_x$ structures were incorporated in a MOS structure. During the plasma treatment, the Si wafers were heated up to 300 °C. SiO$_x$ layers with a thickness of about 9 nm were formed by thermal oxidation at 850 °C. As a tool in the studies, multiple frequency C-V and G-V measurement techniques were used.

2. Experimental details
2.1. Sample preparation
The structures investigated were MOS capacitors formed on 5-10 Ω cm n-type (111)-oriented single-crystal Si wafers. The Si substrates were cleaned using a standard RCA procedure (H$_2$SO$_4$/H$_2$O$_2$ solution followed by a dip in diluted HF and a rinse in deionized H$_2$O). Some of the substrates were subsequently hydrogenated by exposure to RF hydrogen plasma in a planar plasma unit. The RF generator (13.56 MHz) was capacitively coupled to the reactive chamber and delivered input power of 15 W. The hydrogen gas pressure was 133 Pa. The substrates were kept on the lower electrode. Part of the substrates was hydrogenated without heating; other substrates were heated to a 300 °C. The plasma exposure duration was 15 min. Some of the wafers were left with RCA cleaning only, to serve for comparison revealing the effect of hydrogenation and possible advantages of the plasma technology proposed; these samples are referred to below as RCA oxides. Oxides with a thickness of about 9 nm were grown on RF plasma hydrogenated Si by thermal oxidation at 850 °C in dry O$_2$ ambient. The thickness of the SiO$_x$ layers, determined by ellipsometric measurements, varied depending on the conditions of the pre-oxidation treatment, the hydrogenation level at different temperatures, or the wet RCA, but was in the nanoscale range. For electrical characterization, Al dots with a density of 1.96x10$^3$ cm$^{-2}$ on the oxide surface and a continuous Al film on the Si back-side were deposited by vacuum evaporation to form MOS structures.

2.2. Measurements
We obtained information on the concentrations of the electrically-active defects and their location in the Si/SiO$_x$ interface region by analyzing the multiple frequency dispersion of the capacitance-voltage C-V and conductance-voltage G-V characteristics taken at room temperature in the frequency range from 1 kHz to 300 kHz and a 30-mV test signal. The measurement device used was a Wayne-Kerr 6425 Precision Component Analyzer. The interface trap density $D_i(E)$ was evaluated by the standard high-frequency method and by comparing the experimental and the ideal theoretical $C-V$ characteristics curves of the MOS structures [7]. The two-frequency method was developed to explore thin and/or leaky oxides [8]. The energy spectra of the interface traps $D_i(E)$ were obtained by comparing the experimental and the generalized $C-V$ curves. The MOS capacitor was modelled as a three-element circuit. Thus, the generalized frequency-independent $C-V$ curve was evaluated.

Using the values measured on the $C-V$ and $G-V$ curves at two frequencies in the range 1 kHz – 300 kHz, the dissipation $D$ was calculated from

$$D = \frac{G}{\omega C},$$

(1)
where \( G \) is the parallel conductance and \( C \) is the capacitance measured at the different frequencies. From the method presented by Yang and Hu [8] the generalized capacitance \( C' \) is

\[
C' = \frac{f_1^2 C_1(1+D_1^2)-f_2^2 C_2(1+D_2^2)}{f_1^2-f_2^2},
\]

where \( C_1 \) and \( D_1 \) refer to the values measured at the frequency \( f_1 \), and \( C_2 \) and \( D_2 \), to the values measured at the frequency \( f_2 \).

Additional information about the oxide and the interface region with the Si was obtained using a Rudolf Research spectroscopic ellipsometer in the wavelength range 280 – 820 nm at an incidence angle of 70°. The thickness was determined with an accuracy of ± 0.2 nm. The capacitance evaluated from the \( C-V \) curves and the values measured by the ellipsometer were used to calculate the thickness and dielectric constants of the oxide layers. The refractive index was calculated assuming the oxide-Si as being a single-oxide layer system.

3. Results and discussion

The analysis of the electrical characteristics showed that the MOS structures with a SiO\(_x\) layer grown on Si treated in plasma without heating exhibit a hysteresis effect indicating the presence of traps spatially distributed into the oxide near the interface. The shift and the shape of the curves revealed small oxide charge and low leakage currents, i.e., a high-quality dielectric layer.

We applied the two-frequency method of obtaining the \( C-V \) and \( G-V \) characteristics [8] at frequencies ranging from 1 kHz to 300 kHz and generated the generalized \( C-V \) curve for every sample. In this curve, the series resistance and the leakage through the oxide layer are taken into account. The generalized \( C-V \) curves for all samples examined are presented in figure 1.

![Graphs](image_url)

**Figure 1.** \( C-V \) and \( D-V \) curves at two frequencies and generalized \( C-V \) curve (C-corr) for oxides grown on a) Si hydrogenated without heating; b) Si hydrogenated at 300 °C; c) non-hydrogenated Si.
The role of the plasma pre-oxidation treatment on the electrically-active interface defects is illustrated in figures 1a and 1b for MOS structures with oxides grown on plasma-exposed substrates without heating, or heated at 300 °C, respectively. The shape of the curves of plasma-treated Si shows variations typical of a relatively high density of interface traps. In the shape of the curves of Si oxides hydrogenated without heating (figure 1a) and at 300 C (figure 1b), deviations are observed from the ideal shape, typical for a high density of interface traps, even higher than for the oxide of non-hydrogenated Si (figure 1c).

Hydrogenation of the Si wafers at 300 °C results in oxide with C-V and generalized C-V curves with a regular shape, as seen in figure 1b. The C-V curves of this sample are also steeper in comparison to the C-V curves of the oxides on Si not heated during the plasma hydrogenation, which indicates an overall lower density of traps, which can be attributed to the higher degree of an annealing or passivation effect.

The energy spectra of the interface traps D_n over the Si bandgap were calculated for the idealized case without the presence of interface traps over Si bandgap by comparing the generalized C-V curves with the theoretical C-V curves. The results for all oxides grown on hydrogenated without heating, hydrogenated at 300 °C and non-hydrogenated Si substrates are shown in figure 2. As can be seen, the interface trap density spectra show the presence of interface traps with localized energy levels in the Si bandgap. The overall high density of traps in all samples is not unexpected bearing mind the low oxidation temperature and the fact that the oxides were not subjected to any post-oxidation anneals. For all samples, the densities of the interface traps around midgap are less than 3×10^{12} eV^{-1} cm^{-2}. Also, the spectrum of the oxide grown on non-hydrogenated substrate reveals a set of energy levels in the Si bandgap with a relatively high density near the conduction band edge. It should be noted that this oxide has not been subjected to any heat treatment to reduce the trap density.

The localized interface levels for the hydrogenated samples are observed at approximately the same energy positions in the bandgap, with few exceptions, as compared to the non-hydrogenated samples. The oxide grown on hydrogenated Si shows a decrease of the density near the midgap. The position and density of the interface trap levels depend on the hydrogenation temperature of the Si substrate and are assumed to be related to particular structural defects at the interface and in a very thin region within the oxide. In the case of the oxide grown on a Si substrate heated to 300 °C during plasma hydrogenation, the density of the traps decreases even more than in the non-hydrogenated and hydrogenated without heating cases. The explanation could be due to the combined effect of the plasma, the higher temperature of the Si substrate and the incorporation of the hydrogen during the hydrogenation in the plasma, which serves to restore the destroyed chemical bonds in the interface region. For the oxide grown on a Si substrate hydrogenated without heating, although showing a positive effect as seen in figure 2, the inclusion of hydrogen only is not sufficient to reduce the density of the traps compared to the oxide grown on non-hydrogenated substrate.

The localized trap levels observed in the Si bandgap can be associated with the interface region where a transition from crystalline Si to amorphous silicon oxide occurs. It can be assumed that the oxide layer is not stoichiometric SiO_2, because the low oxidation temperature is insufficient for growing oxide with complete Si oxidation. The presence of hydrogen in the hydrogenated Si layer influences the mechanism of oxide growth and, hence, its structure. This is why in the interface spectra there appears a set of distributed localized states due to deformed bonds, rather than single
levels. The latter are usually attributed to a well-defined dangling bond at the interface of Si with high-
temperature SiO$_2$.

For all samples, two peaks in the interval 0.05±0.2 eV are evident at an energy position in the upper
half of the bandgap, the one closer to $E_c$ being with higher intensity, with the exception of the sample
hydrogenated at 300 °C. Theoretically [9], these interface defect centers are considered oxygen
cavities and weak Si-Si bonds that appear energetically in this region. The peak at about 0.4 eV,
observed for hydrogenated samples, could be linked to dangling Si-bonds, again based on the same
theoretical and experimental results [9].

An interesting effect is the peak around the midgap found in the non-hydrogenated sample and in
the sample hydrogenated at 300 °C, usually attributed to the dangling Si-bonds [9]. A peak at 0.68 eV
is also observed, which is characteristic of the non-hydrogenated sample and the one hydrogenated at
300 °C and can be ascribed to weak Si-O bonds.

The basic oxide parameters characterizing the MOS structures, such as the oxide thickness,
refractive index, oxide stress and width of the transitional interface region are given in table 1. These
parameters resulting from ellipsometric measurements indicate that grown oxides must be regarded as
SiO$_x$, where $x < 2$. The values of the refractive index at 633 nm for the oxides exceed 1.46, as
isotypical of nonstoichiometric SiO$_x$. For our oxides, $x$ was estimated from simulated data for the
refractive index for SiO$_x$ by varying the oxygen content [10]. The results are given in the table. Similar
values for $x$ were also found for SiO$_x$ films deposited by reactive sputtering [11]. These refractive
index values are higher as compared to stoichiometric SiO$_2$ and substantially lower than for Si
monoxide. This implies that the oxide composition can be characterized rather as sub-stoichiometric
SO$_2$ with $x < 2$.

The thickness of the SiO$_2$ layers, calculated from the ellipsometric data, varied around ~ 9 nm,
depending on the pre-oxidation treatment, either RCA cleaning or plasma exposure. The oxides grown
on plasma exposed substrates showed slightly greater thicknesses, as already observed in our previous
studies [12]. This can be explained by the fast growth of the first monolayers of SiO$_2$ due to the
presence of a plasma-modified surface layer in the Si substrate. This layer has been suggested to
contain hydrogen decorated voids [13]. The refractive indices were higher than 1.46, the value typical
for stress-free oxide.

| Si wafer pre-oxidation treatement | Refractive index n | Oxide thickness $d_{ox}$ (nm) | Dielectric constant $\varepsilon$ | $\sigma.10^8$ (N/m$^2$) | $x$ |
|-----------------------------------|-------------------|-------------------------------|-------------------------------|-------------------|-----|
| Plasma hydrogenation:              |                   |                               |                               |                   |     |
| unheated                          | 1.458             | 9.54                          | 3.24                          | 3.1               | 1.35|
| Plasma hydrogenation: 300°C       | 1.490             | 9.19                          | 3.69                          | 2.0               | 1.33|
| Without hydrogenization           | 1.580             | 8.30                          | 3.70                          | 4.0               | 1.25|
| SiO$_2$                           | 1.460             | -                             | 3.90                          | -                 | 2.00|
| SiO                               | 1.960             | -                             | 5.00                          | -                 | 1.00|

The dielectric constants of the oxides were calculated from the capacitance in strong accumulation
of the generalized C-V curves. The results for the dielectric constant of the oxide are also summarized
in the table. For comparison, the table also presents data for $\varepsilon$ and $n$ of stoichiometric SiO$_2$ and SiO
[12, 13, 14]. From the data for the dielectric constant, one can also draw conclusions about the oxides
structure. One could assume that the lower dielectric constants are due to the presence of voids ($\varepsilon = 1$)
in the upper Si-layer formed during the hydrogenation plasma, which persist even after oxidation [15].

The parameters of oxides on hydrogenated Si can also differ from those of oxides grown on non-
hydrogenated Si before oxidation, as evidenced by the data in from the table.
4. Conclusions

Conclusions on the quality of the oxide and the interface to the Si substrate were drawn from the results of the electrical characterization performed on silicon oxides grown on RF plasma hydrogenated Si. The densities of the interface traps, as evaluated from C-V and G-V measurements using a two-frequency technique to generate frequency and leakage independent curves, depend on the degree of hydrogenation. The C-V and G-V analysis demonstrated the generation of localized interface traps due to dangling Si bonds and to weak and distorted Si-O bonds. A series of localized states acting as interface traps was found that characterize the interface of Si as a sub-stoichiometric SiO\textsubscript{x} layer. For the oxide grown on hydrogenated Si at higher wafer temperature, most of the traps were annealed. The dielectric constants were determined from generalized C-V curves. We believe that the oxides grown on hydrogenated Si are non-stoichiometric and contain voids that reduce the dielectric constant. We further concluded that the density of interface defects can be optimized by heating the Si to 300°C during plasma hydrogenation.

References

[1] Ran G Z, Chen Y, Yuan F C, Qiao Y P, Fu J S, Ma Z C, Zong W H and Qin G G 2001 Solid State Commun. 118/11 599-602
[2] Swain B S, Swain B P, Lee S S and Hwang N M 2012 J. Phys. Chem. C 116/41 22036-42
[3] Qian K K and Bogner R H 2012 J. Pharm. Sci. 101 444-63
[4] Saraswat K How far can we push Si CMOS? http://www.ohio.edu/people/starzyki/network/class/ee516/slides/Future%20Devices.pdf
[5] Iwai H 2013 Ultimate CMOS scaling Proc. Korean Int. Summer School on Nanoelectr. (2–5 July 2013 Daejon Korea) http://www.iwailab.ep.titech.ac.jp/pdf/iwaironbun/201307nanokiss.pdf
[6] Balestra F 2014 Beyond CMOS Nanodevices (Wiley & Sons – Interscience, New York)
[7] Nicollian E H and Brews J R 1982 MOS Phys. and Technol. (Wiley, New York)
[8] Yang K J and Hu Ch 1999 IEEE Trans. Electron Dev. 46 1500
[9] Flietner H 1985 Phys. Stat. Solidy A 91 153–7
[10] Tomozeiu N 2011 Silicon oxide (SiO\textsubscript{x}, 0 < x < 2): a challenging material for optoelectronics, Optoelectronics - materials and techniques ed Predeep P
[11] Miyazaki H 2010 Phys. Chem. of Glasses - European J. Glass Sci. Technol. B 51 136
[12] Szekeres A, Alexandrova S, Lytvyn P and Kompitsas M 2005 J. Phys.: Conf. Series 10 246
[13] Asoka-Kumar P, Stein H J and Lynn K G 1994 Appl. Phys. Lett. 64 1684
[14] Szekeres A, Paneva A, Alexandrova S, Lisovskyy I, Litovchenko V and Mazunov D 2003 Vacuum 69 355
[15] Kaschieva S, Halova E, Vlaiikova E, Alexandrova S, Valcheva E and Dmitrov S 2006 Plasma Process. Polym. 3 237