Electrical parameters of thin nanoscale SiO$_x$ layers grown on plasma hydrogenated silicon

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Abstract. In the present paper results are presented on electrical characterization of the interface Si/SiO$_x$, formed by oxidation on Si wafers, previously exposed to rf hydrogen plasma. As a tool of investigations multiple frequency $C$-$V$ and $G$-$V$ measurements are applied. The data analysis was performed using two-frequency method to extract generalized frequency independent $C$-$V$ characteristic. Interface trap densities were evaluated from the generalized $C$-$V$ data by comparison with theoretical data for an ideal interface. A set of localized states, acting as interface traps, was found that characterize the interface of Si to substoichiometric SiO$_x$, layer with $x < 2$. The dielectric constant of the oxides was calculated from the capacitance in accumulation of the generalized $C$-$V$ curves. The thickness and the refractive index of the oxide layers were obtained from ellipsometric data analysis assuming the oxide-Si substrate as single layer system. From the data for the dielectric constant and refractive index suggestion is made that the grown oxides on hydrogenated Si contain voids thus reducing the dielectric constant. Correlation with oxide mechanical stress is found.

1. Introduction

Contemporary semiconductor electronics is still largely dominated by the silicon technology. Reaching Si CMOS limits, great efforts have been exerted to search for a replacement of the SiO$_2$ by other dielectric layer with higher dielectric constants, to design different gate structures or even to develop entirely different materials for non-Si based electronic elements. However, still no reasonable candidate has been found to replace the thermally grown SiO$_2$ with its high dielectric quality and perfect interfaces. Si will continue to be the main substrate due to its overall excellent properties. Beyond for CMOS digital applications, Si/SiO$_2$ has been used for applications in various structures from solar cells to graphene films and carbon nanotubes, new 2D geometry, double gate devices, ballistic nanotube transistors etc. Detailed discussion on future developments of nanodevices can be found in the recent reviews [1, 2, 3]. It can be concluded that at least in the next decade Si/SiO$_2$ will remain as an important building block.

Small sized silicon oxide in nanodevices obtained either by thermal oxidation of Si or by some deposition technique is usually non-stoichiometric SiO$_x$. Thermal oxidation is conducted at lower temperatures compromising film growth rate and film quality. The interface to the Si can reveal lower quality, higher gate leakage and interface trap density. Improvement can be achieved by incorporation of hydrogen. Heating in hydrogen containing atmosphere has been widely used the past decades due to...
different beneficial effects such as stabilization of device characteristics through gettering of impurities and saturation of defects. Applied to silicon oxide layers in the nanometric scale, hydrogenation can have a beneficial impact for improving the defect and leakage characteristics.

Our previous studies have shown that hydrogenation of Si before thermal oxidation has a potential for obtaining higher interface quality to ultrathin oxides with thickness around and below 15 nm [4]. An optical study using micro-Raman and spectral ellipsometry revealed the possibility to control the mechanical stress in the Si below the interface [5]. The possible future application of the thin films grown on the hydrogenated Si is conditional upon the studying of their electrical properties. Express and well developed technique for characterization is the capacitance-voltage $C-V$ method. Combined with conductance-voltage $G-V$ measurements taken at different frequencies it can deliver valuable information about interface quality.

The aim of the present paper is electrical characterization of the Si/SiO$_x$ interface, formed on Si wafers exposed to rf hydrogen plasma prior oxidation. During plasma hydrogenation the Si wafers could be heated up to 300ºC. The SiO$_x$ layers with thickness below 10 nm were formed by thermal oxidation at 850ºC. Thickness was ellipsometrically controlled.

For electrical characterization purposes the Si/SiO$_x$ structures are incorporated in a MOS device. As a tool of investigation multiple frequency $C-V$ and $G-V$ measurement techniques are applied.

2. Sample preparation
The structures used in this study were MOS capacitors formed on 5-10 Ohm.cm $n$-type (111)-oriented single-crystal Si wafers. Oxides with a thickness below 10 nm were grown on rf plasma hydrogenated Si by thermal oxidation at 850ºC in dry O$_2$ ambient. The Si wafers 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 de-ionized H$_2$O). Some of the substrates were subsequently hydrogenated by exposure to a rf hydrogen plasma in a planar plasma unit. The rf generator (13.56 MHz) was capacitively coupled to the reactive chamber with an 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 and for another part the temperature was 300ºC. Duration of the plasma exposure was 15 min.

The oxidation was performed in same oxidation run for all substrates, the plasma exposed and those with treated in RCA only. The oxides grown on RCA cleaned samples served for comparison, to reveal the effect of hydrogenation and possible advantages of the proposed plasma technology as well.

For electrical characterization 1.96x10$^{-3}$ cm$^2$ Al dots on the oxide surface and Al continuous film on the Si back-side were deposited by vacuum evaporation to form MOS structures. Information about the concentrations of the electrically active defects was gained from analysis of the frequency dispersion of the $C-V$ and $G-V$ characteristics taken at room temperature in the frequency range 1 Hz - 300 kHz. The measurement unit was a Precision Component Analyzer Wayne-Kerr 6425. The interface trap density $D_{it}$ was evaluated by comparison of the experimental and ideal theoretical $C-V$ characteristics. For that purpose a two frequency method has been applied [6] developed to explore thin and/or leaky oxides. The MOS capacitor is modelled as a three-element circuit. By this technique a generalized frequency independent $C-V$ curve is evaluated.

Using the measured $C-V$ and $G-V$ curves at two frequencies in the range 1Hz - 300 kHz the dissipation $D$ is calculated from

$$D = \frac{G}{\omega C}$$  \hspace{1cm} (1)

where $G$ is the parallel conductance and $C$ is the capacitance measured at the different frequencies.

Using the method presented by Yang and Hu [6] 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 values measured at the frequency \( f_1 \) and \( C_2 \) and \( D_2 \) refer to values measured at the frequency \( f_2 \). where \( C_1 \) and \( D_1 \) refer to values measured at the frequency \( f_1 \) and \( C_2 \) and \( D_2 \) refer to values measured at the frequency \( f_2 \).

Figure 1. \( C-V \) and \( D-V \) curves at different frequencies and generalized \( C-V \) characteristics

- (a) Si hydrogenated without heating;
- (b) Si hydrogenated at 300ºC;
- (c) Si unhydrogenated.

Additional information about the oxide and interface region to the Si was gained using a Rudolf Research spectroscopic ellipsometer, in the wavelength range 280-820 nm, at an incidence angle of 70º. The accuracy of the thickness determination was ± 0.2 nm. The refractive index was calculated assuming the oxide-Si as a single oxide layer system. The mechanical stress across the oxide was evaluated from analysis of the spectra gained by micro-Raman spectroscopy (RS).

3. Results and Discussion

The analysis of the electrical characteristics has revealed that the MOS structures with SiO\(_x\) layer grown on hydrogenated Si indicate shifts and shapes of the measured curves that refer to small oxide charge and low leakage currents, i.e. high quality dielectric layer. Applying two-frequency method to the \( C-V \) and \( G-V \) characteristics taken at a variety of frequencies [6], a generalized \( C-V \) curve for every
sample was generated. In these curves the series resistance and the leakage through the oxide layer is accounted for. The generalized \( C-V \) curves are displaced in figure 1.

The shape of the curves for oxides on Si hydrogenated without heating (figure 1a) shows variations typical for high density of interface traps, even higher than the oxide on unhydrogenated Si (figure 1c). Hydrogenation of the Si wafer at 300ºC ensures oxide with \( C-V \) and \( G-V \) curves with more regular shape (figure 1b).

From comparison of the generalized \( C-V \) curves with the theoretical \( C-V \) curves, calculated for idealized case without presence of interface traps, the energetic spectra of the interface traps over Si bandgap have been calculated. The results for the oxides grown on hydrogenated and unhydrogenated Si wafers are given in figure 2. The spectra show the presence of interface traps with localized energy levels in the Si bandgap. It can be seen that the spectrum of the oxide grown on unhydrogenated substrate reveals a set of energetical levels in the Si bandgap and a steep increase near the conduction band edge with relatively high density. It should be remembered that this oxide has not been subjected to any thermal treatment for trap concentration decrease. The oxide grown on hydrogenated Si shows decrease of the density near midgap. Localized interface levels appear similarly to oxide on unhydrogenated Si and approximately at same energetical positions in the band. Results concerned to the oxide grown on a Si substrate that has been heated up to 300ºC during plasma hydrogenation are also presented. It can be seen that in this case the spectrum flattens, localized states have disappeared, the density of the traps is reduced. The explanation could be in the combined annealing effect of the increased temperature and hydrogen incorporated during plasma hydrogenation which serves to repair damaged chemical bonds in the interface region. Hydrogen supply only, as evident from the spectrum of the oxide grown on Si hydrogenated without heating, although showing beneficial effect, is still not sufficient to bring the density of the traps to substantially low level. Localized trap levels in Si bandgap can be associated to the interface region where transition from the crystalline Si to the amorphous silicon oxide occurs. Most probably the oxide layer is not stoichiometric SiO\(_2\) because of the oxidation temperature that is much below the condition for growing oxide with complete oxidation of the Si. The growth mechanism of the oxide, and consequently, its structure, is influenced by the presence of hydrogen in the hydrogenated Si top layer. For that reason in the interface spectra appears a set of localized states due to deformed bonds, not necessarily the single levels that are usually contributed to well defined dangling bonds at the interface of Si with high temperature SiO\(_2\).

Data from ellipsometric study also indicates that the grown oxides should be defined as SiO\(_x\), where \( x < 2 \). The refractive index values at 633 nm for the oxides are over 1.46 which is typical for stoichiometric SiO\(_2\). Taking the thickness of the oxide layers from the ellipsometric data, the dielectric constant of the oxide was calculated from the capacitance in strong accumulation of the generalized \( C-V \)
$V$ curves. The results for the refractive index and the dielectric constant of the oxides are summarized in the table.

Table. Parameters of oxides grown on Si with different pre-oxidation treatment.

| Si wafer pre-oxidation treatment | Refractive index $n$ | Oxide thickness $d_{ox}$ [nm] | Dielectric constant $\varepsilon$ $\sigma \times 10^8$ [N/m²] | $\rho/M$ [mol/cm⁻³] |
|---------------------------------|----------------------|-----------------------------|---------------------------------|-------------------|
| Plasma hydrogenation: unheated   | 1,620                | 13,60                       | 3,76                            | 1,94              | 0,0476            |
| Plasma hydrogenation: 300°C      | 1,478                | 13,20                       | 3,42                            | 1,80              | 0,0381            |
| Without hydrogenation           | 1,468                | 14,12                       | 3,73                            | 2,48              | 0,0374            |
| SiO$_2$                         | 1,460                | -                           | 3,90                            | -                 | 0,0368            |
| SiO                             | 1,960                | -                           | 5,00                            | -                 | 0,2760            |

For comparison, in the table data for $\varepsilon$ and $n$ is given for stoichiometric SiO$_2$ and silicon monoxide SiO [7, 8, 9]. However, oxide parameters can depend on oxide thickness and be different from those for bulk relaxed material. The parameters for oxides on hydrogenated Si can differ also from those of oxides grown on unhydrogenated Si before oxidation, which is evident from the table.

It can be expected that the dielectric constant $\varepsilon$ should fall between the values of 3,9 for stoichiometric SiO$_2$ and 5 for silicon monoxide. However, our results are below this interval. The refractive index data reveal higher values as compared to stoichiometric SiO$_2$ and substantially lower values than SiO monoxide. This implies that the oxide composition can be characterized rather as substoichiometric silicon dioxide, which becomes clearly evident for the oxides on plasma hydrogenated Si wafers being more pronounced for hydrogenation without heating. From the data for the dielectric constant also further indications can be made about the structure of the oxides. It can be suggested that the films contain voids with $\varepsilon = 1$, which lowers the dielectric constant. The voids have been proposed to be created in Si top layer during plasma hydrogenation which persist even after oxidation [4]. Inclusion of voids in oxide network would imply smaller film density. Next, the film density can be extracted from the refractive index by using the Lorentz-Lorenz relation:

\[
\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N \alpha \frac{\rho}{M}
\]

where $n$ is the index of refraction, $M$ is the molecular mass, $\rho$ is the mass density, $N$ is Avogadro’s number $6,022 \times 10^{23}$ mol⁻¹ and $\alpha$ is the total polarizability of the molecule. However, without specific composition data for the film, calculation of its density is not possible. Since the composition of the investigated oxides is expected to be SiO$_x$, where $x$ varies from 1 to 2, the molecular mass of the film is between 44,08 g/mol for silicon monoxide and 60,08 g/mol for SiO$_2$ and the density between 2,13 g/cm$^3$ and 2,2 g/cm$^3$, respectively. Some insight to the dielectric constant dependence on the structure and composition of the oxide can be gained from the $\rho/M$ ratio. Substituting the data for the refractive index $n$ and taking the total polarizability $\alpha = \alpha_e$ (electron polarizability) = $2,95 \times 10^{-34}$ cm$^3$ [10] results for $\rho/M$ are obtained and included in the table. Again it can be concluded that the oxides are substoichiometric silicon oxides with $x < 2$. The ratio $\rho/M$ is higher than the value for relaxed SiO$_2$ but
much smaller than for SiO. It should be remembered that the oxide parameters, dielectric constant, refractive index, mass density and interface trap density depend not only on composition, but on thickness as well [11, 12] For oxides grown thermally on Si at 1000°C [11] with similar thickness as in the present study, the density amounts to about 4 g/cm³ corresponding ρ/M = 0.0666 for SiO₂ composition, as suggested by the authors.

Further indication on the composition and structure of the oxides comes from the data for the mechanical stress over the oxide as gained from micro-Raman analysis. The stress generated from oxidation process only for the oxides on RCA treated Si shows relatively high value. Preoxidation hydrogenation of the Si obviously leads to relaxation of the stress mainly through creation of voids retained after oxidation.

4. Conclusions
Electrical characterization of silicon oxides grown on rf plasma hydrogenated Si was conducted. Interface trap densities were evaluated from C-V and G-V measurements taken at different frequency applying two-frequency technique. A set of localized states acting as interface traps was found that characterize the interface of Si to substoichiometric SiOₓ layer. For oxide grown on Si hydrogenated at increased wafer temperature most of the traps are annealed out. The traps should be due to deformed bonds, not necessarily the single levels that are usually contributed dangling Si bonds at the interface of Si with high temperature SiO₂. The dielectric constants were extracted from the generalized C-V curves. Suggestion is made that the grown oxides on hydrogenated Si contain voids thus reducing the dielectric constant. Correlation is found with the results from ellipsometrically obtained refractive index and its relation to oxide mass density. The mechanical stress on the oxide estimated from micro-Raman evaluation shows decrease due to presence of voids in the oxide. Conclusion is made that the oxides grown on plasma hydrogenated Si can be characterized as substoichiometric SiOₓ layers.

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