Interface characterization of nanoscale SiOx layers grown on RF plasma hydrogenated silicon

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Abstract. In the present paper, results are presented on electrical characterization of the interface Si/SiOx, formed by oxidation on Si wafers previously exposed to rf hydrogen plasma. As tools of investigations, multiple frequency C-V and G-V measurements were applied. The data analysis was performed using a two-frequency method to extract a generalized frequency independent C-V characteristic. The 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 SiOx, 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 being a single layer system. From the data for the dielectric constant and refractive index, the suggestion is made that the oxides grown on hydrogenated Si contain voids thus reducing the dielectric constant. Correlation with oxide mechanical stress is found.

1. Introduction

Control and characterization of the defects at the interfaces in single or multilayered structures is an important issue in modern semiconductor devices. The incorporation of hydrogen into a semiconductor structure is known for its beneficial effect, namely, stabilization of device characteristics mainly through gettering of impurity defects. In silicon technology, hydrogenation has been widely used in the past decade in lower concentrations for improving the defect and leakage characteristics, and in higher concentrations for future nanoelectronic applications, such as exfoliation of silicon in smart cut process, increase of carrier life time in solar cells, etc.

Contemporary semiconductor electronics is still largely dominated by the silicon technology. 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. A detailed discussion on future developments of nanodevices can be found in the excellent reviews [1, 2, 3]. It can be concluded that at least in the next decade Si/SiO_2 will remain an important building block.

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The aim of the present work is characterization of the interface between rf plasma hydrogenated (100) p-Si wafers and the overgrown nanoscale SiO_x by thermal oxidation at 850°C. The interface traps density spectra are assumed to depend on the amount of incorporated hydrogen. For this purpose, plasma hydrogenation of the Si wafers was conducted either without heating of the Si substrate or heating them up to 300 °C; the interface traps density spectra were examined in detail.

2. Experimental details

2.1 Sample preparation

The MOS capacitors investigated in this work were formed on substrates of p-type (100)-oriented single-crystal Si wafers, 5-10 Ohm cm. The Si wafers were initially cleaned using H_2SO_4/H_2O_2 solutions by standard wet RCA pre-gate oxide cleaning followed by a dip in diluted HF and a rinse in deionized H_2O. Parts of the wafers were subsequently hydrogenated by exposure to a rf hydrogen plasma in a planar plasma unit at 13,56 MHz, gas pressure of 133 Pa and input power of 15 W. The substrates were kept on the lower electrode. The duration of the plasma exposure was 15 min. The hydrogenation was performed on Si wafers, either unheated or at 300 °C. Other wafers were left with RCA cleaning only, to serve as a reference, and will be referred to as RCA oxides. The differently cleaned wafers were thermally oxidized at 850 ℃ by exposing to dry O_2 flow in a conventional atmospheric furnace. The thickness of the SiO_x layers varied depending on the conditions of the pre-oxidation treatment, the hydrogenation level at different temperatures or wet RCA, but was in the nanoscale range below 10 nm, as determined from the ellipsometric measurements. In order to obtain information about the charged states in the structures, the oxides were incorporated in MOS capacitors formed by thermally-evaporated circular aluminum contacts with an area $1,96\times10^{-3}$ cm^2 on the SiO_x surface using a mechanical mask, and a continuous Al layer on the back side of the substrates.

2.2 Measurements

Information on the concentration of the charged defects and their location in the Si/SiO_x interface region was obtained by using multiple frequency capacitance-voltage (C-V) and conductance-voltage (G-V) measurement techniques. The measurement unit was a Precision Component Analyzer Wayne-Kerr 6425. Applying the two-frequency method to the C-V and G-V characteristics taken at various frequencies ranging from 500 Hz to 300 kHz and a 30-mV test signal, at room temperature, a generalized C-V curve was generated.

The density of interface trap $D_{it}(E)$ profiles in the Si bandgap was investigated by the standard high-frequency method of obtaining C-V characteristics of the MOS structures and comparing the experimental curve with the ideal theoretical one [4]. For that purpose, a two-frequency method was developed and applied [5] to explore thin and/or leaky oxides. The energy spectra of the interface traps $D_{it}(E)$ were extracted from comparison of the experimental and the generalized C-V curves. The three-element circuit model of a MOS capacitor was used. This technique allowed the evaluation of a generalized frequency independent C-V curve.

From the measured values of C-V and G-V curves for two frequencies in the range 500 Hz - 300 kHz, the dissipation D is calculated from the formula

$$D = \frac{G}{\omega C}, \qquad (1)$$

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

Based on the method of Yang and Hu, presented in [5], the generalized capacitance C' is
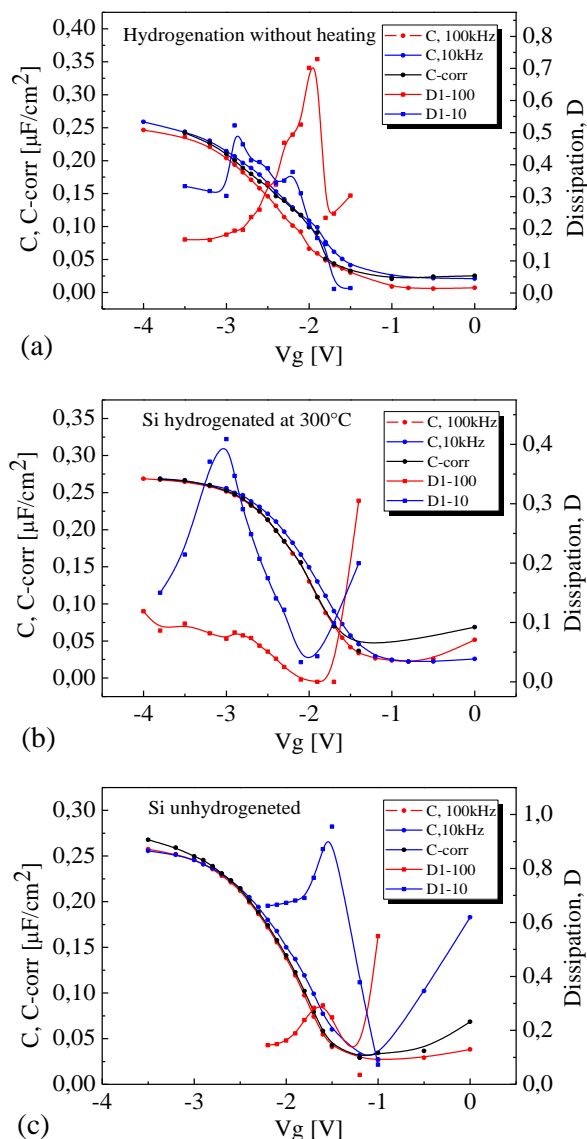
$$C' = \frac{f_1^2 C_1(1+D_1^2) - f_2^2 C_2(1+D_2^2)}{f_1^2 - f_2^2}, \qquad (2)$$

where C_1 and D_1 are the values measured at the frequency f_1 and C_2 and D_2 are the values measured at the frequency f_2.

Additional information about the oxide and the interface region to the Si was acquired using a Rudolf Research spectroscopic ellipsometer, in the wavelength range 280-820 nm and at an incidence angle of 70º. The accuracy of the thickness determination was ± 0,2 nm. The ellipsometric data and the capacitance in strong accumulation of the C-V curves used used for calculation of the thickness and the dielectric constants of the oxide layers. The refractive index was calculated assuming the oxide-Si as a single oxide layer system.

3. Results and discussion

By applying the two-frequency method to the C-V and G-V characteristics taken at various frequencies [5], generalized C-V curves for all samples were generated. In these curves, the series resistance and the leakage through the oxide layer is accounted for.v Figure 1 presents the generalized C-V curves. The study of the electrical characteristics showed that the MOS structures with SiO_x layer grown on hydrogenated Si exhibit shifts and shapes of the measured curves that refer to a small oxide charge and low leakage currents, i.e., a high-quality dielectric layer.

The shape of the curves of plasma-treated Si without heating shows variations typical of a high density of interface traps. In the shape of curves of Si oxides hydrogenated without heating (figure 1a), one observes deviations from the ideal shape, typical for a high density of interface traps, even higher than the oxide of the unhydrogenated Si (figure 1c). Hydrogenation of the Si wafer at 300 °C results in an 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 unheated 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 interface traps density was calculated over the Si bandgap using the distributions D_{it} obtained from comparison of the generalized C-V curves with the theoretical C-V curves, calculated for the idealized case without the presence of interface traps. The results for all oxides grown on differently treated Si wafers prior to oxidation are presented in figure 2. The densities around midgap are below 10^{12} eV^{-1} cm^{-2} for all oxides. The interface density spectra show the presence of localized interface traps energetically distributed in the Si bandgap. Localized interface levels appear approximately at the same energy positions in the bandgap for the oxides grown
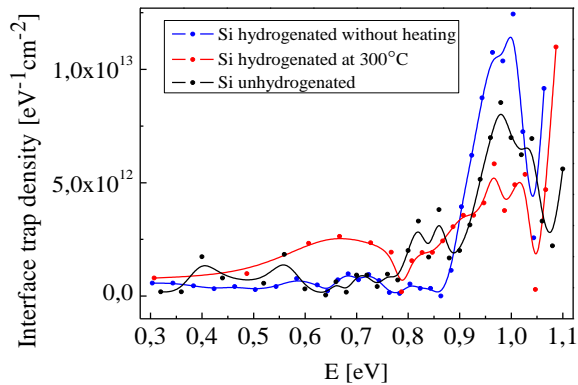

Figure 1. C-V and D-V curves at different frequencies and generalized C-V curve (C-corr) for oxides grown on a) Si hydrogenated without heating; b) Si hydrogenated at 300 °C; c) unhydrogenated Si.

Figure 2. Interface trap density spectra.

on hydrogenated and unhydrogenated Si wafers. The positions and the density of the trap levels depend on the hydrogenation temperature of the substrate and are assumed to be related to particular structural defects at the interface and in a thin region inside the oxide.

It is known that the dangling Si bonds form a peak at 0,82 eV above the valence band edge E_v [6]. A double peak at about this position is seen most clearly in our oxides on unhydrogenated Si wafers. Generation of defects is often related to intrinsic interface stress of $Si = SiO_2$ [7]. For our oxides, the stress levels as obtained by ellipsometric measurement [8] are presented in the table. Another double peak found in all oxides around 0,97 eV near E_v can be attributed to vacancy-oxygen (V/O) complex defects. A localized interface trap level was found near this energy position in irradiated SiO_2 [9]. It can be seen that in the oxide grown on a Si substrate that has been heated up to 300ºC during plasma hydrogenation, the density of the traps is reduced. A higher trap density in this region has an important contribution to the flatband and threshold voltage values so that the reduction of the density of traps is an important result. Over the rest of the Si bandgap, the density is close for all studied oxides. Moreover, the oxides grown on unhydrogenated Si exhibit a set of levels around midgap which disappear in oxides on hydrogenated Si and the spectra flatten. The explanation of the behavior of the interface traps can be found in the combination of annealing effect at the increased temperature and hydrogen incorporated during the plasma hydrogenation, which serve for the reconstruction of chemical bonds in the region of the interface.

The results of ellipsometry measurements, summarized in the table 1, also indicates that the grown oxides must be regarded as SiO_x, where $x < 2$. The values of the refractive index over 1,46 are typical of non-stoichiometric SiO_x. For our oxides, x was estimated from simulated data for the refractive index for SiO_x when varying the oxygen content [10]. The results are given in the table 1. Similar values for x were also found for SiO_x films deposited by reactive sputtering [11].

Table 1. 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 ε	$\sigma \times 10^8$ (N/m^2)	x
Plasma hydrogenation: unheated	1,606	13,27	3,63	3,1	1,26
Plasma hydrogenation: 300 °C	1,678	12,57	3,81	2,0	1,16
Without hydrogenation	1,660	12,02	3,64	4,0	1,20
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 using the thickness of the oxide layers from the ellipsometric data. The results for the dielectric constant of the oxide are also summarized in the table. For comparison, additionally in the table the data for ε and n for stoichiometric SiO_2 and silicon oxide SiO are given [12, 13, 14]. 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. The refractive index data

reveal higher values as compared to stoichiometric SiO_2 and substantially lower values than for SiO monoxide. This implies that the oxide composition can be characterized as rather substoichiometric silicon dioxide with $x < 2$. From the data for the dielectric constant, one can also draw conclusions about the structure of oxides. It can be supposed that the lower dielectric constant 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].

4. Conclusions

Electrical characterization of silicon oxides grown on rf plasma hydrogenated Si was studied. The densities of interface traps were evaluated from C-V and G-V measurements taken at different frequencies, using a two-frequency technique to generate independent frequency and leakage curves. The C-V and G-V analysis demonstrated the generation of localized interface traps due to dangling Si bonds, and a vacancy-oxygen (V/O) complex. A series of localized states acting as interface traps was found that characterize the interface of Si as substoichiometric SiO_x layer. Most of the traps were annealed for oxide grown on Si hydrogenated at increased wafer temperature. The dielectric constants were determined from the generalized C-V curves. The suggestion was made that grown oxides on hydrogenated Si contain voids that reduce the dielectric constant. The mechanical stress of the oxide, estimated by ellipsometry, indicated a decrease due to the presence of voids in the oxide. It was concluded that the concentration of interface defects can be optimized by heating the Si to 300 °C during plasma hydrogenation.

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