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Fixed oxide charge, interface traps and border traps in MOS structures, grown on plasma hydrogenated (100)-pSi♣

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The subject of the present study is the interface region of MOS structures with oxides grown on (100)-pSi hydrogenated wafers. The hydrogenation was accomplished in an RF plasma, the Si substrates being either unheated or kept at 300°C. The oxides were thermally grown in dry O_2 at 850°C. Information was gained on the concentration of charged defects and their location in the Si/oxide interface region, from examination of the capacitance-voltage (*C-V*) frequency behaviour. A comparative analysis was performed on the electrically active defects for the structures, with different hydrogenation conditions. The concentrations of border traps were determined by analysis of the hysteresis of the *C-V* curves. The interface trap density profiles over the Si bandgap were investigated by a standard high frequency method from the 300 kHz *C-V* characteristics of the MOS structures. The intrinsic fixed oxide charges were determined from the transition frequencies of the interface trap response separating low from high frequencies for the different samples. The concentration and nature of the defects were found to depend on the substrate temperature during plasma exposure. In oxides on unheated Si, negatively charged oxide defects were found.

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1. Introduction

The pre-oxidation conditions of the Si surface play a decisive role on the growth kinetics of thin dielectric layers and their properties, especially in view of the shrinkage in the size of semiconductor heterostructures. It has been stressed in the International Technology Roadmap for Semiconductors 2007 [1] that special attention has to be devoted to the surface preparation for further growth or deposition of high quality dielectric layers. To meet the challenges of nanosized structures, different approaches have to be developed, including improvements to the traditional wet-cleaning methods.

In the surface preparation steps, many different approaches are under investigation to meet the requirements, including improvements to the traditional wet-cleaning but also development of new approaches. Coordination defects and weak bonds at the surface play a crucial role in the thin film growth of semiconductor and dielectric materials. Recently, we have applied RF hydrogen plasma treatment as Si pre-oxidation cleaning and have established that hydrogen incorporated in the Si near-surface region helps the growth of a better oxide network [2]. An effective increase in the oxidation rate of plasma hydrogenated Si has been found in both (111) and (100)Si; the increase being more significant for (100)Si. The increased rate for (111)Si was accompanied by defect formation, but heating the Si during hydrogenation was an effective tool to achieve defect densities even lower than for single RCA pre-oxidation treatment.

The aim of this work is to study the plasma stabilization of the thin oxide for technologically more significant (100) Si orientation and the definition of optimum conditions concerning the charged defects at the oxide/Si interface. Results are reported from a detailed study of the *C-V* and *G-V* characteristics. From the frequency dispersion and hysteresis effects, information is gained on the concentrations of the charged defects and their location in the oxide/Si interface region. An attempt is made to differentiate between fixed oxide charges, interface traps and the so-called border traps [3]. Border traps can act like either interface traps or bulk oxide traps, depending on the bias and the time scale and their distribution from the interface within the oxide. It must be noted that upon decreasing the oxide thickness, all defects may act as border traps.

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2. Experimental

The substrates - (100) p-Si, 5-10 Ohm.cm - 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. Parts of the wafers were exposed to hydrogen plasma in a planar unit at 13.56 MHz, a gas pressure of 133 Pa and an input power of 15 W. The hydrogenation was performed on Si wafers, either unheated (marked as 20°C) or at 300°C. Other parts were left with RCA cleaning, to serve as a reference, and will be referred to as RCA oxides.

The differently cleaned wafers were thermally oxidized in the same run, by exposing to dry O_2 in a conventional atmospheric furnace. The wafers were brought to the oxidation temperature of 850°C in N_2 and then the O_2 flow was started. After oxidation, the O_2 flow was switched to N_2 and the samples were pulled out to cool down at the end of the furnace. The oxide thickness varied around ~10 nm, depending substantially on the conditions of the pre-oxidation treatment, hydrogenation at different temperatures or wet RCA.

In order to obtain information about the charged states in the structures, the oxides were incorporated in MOS capacitors. For this purpose, circular Al front contacts were thermally evaporated, while the back contacts to the Si substrate consisted of continuous Al layers.

Information on the concentration of the charged defects and their location in the oxide/Si interface region was gained from examination of the room temperature capacitance-voltage (*C-V*) and conductance-voltage (*G-V*) characteristics, recorded at frequencies from 500 Hz to 300 kHz and a 30 mV test signal. The first measurement was taken at 300 kHz and further the measurements were taken in descending order of frequency. The measurement unit was a Precision Component Analyzer Wayne-Kerr 6425. The *C-V* hysteresis was used to estimate the concentration of the border traps N_{st} at the interface. The interface trap density D_{it} profiles in the Si bandgap were investigated by the standard high frequency method from the 300 kHz, and in some cases from the 100 kHz *C-V* characteristics of the MOS structures comparing the experimental curve and the ideal theoretical one [4]. From the transition frequencies of the interface trap response separating low from high frequencies, the intrinsic fixed oxide charge Q_{if} was determined [5].

3. Results and discussion

In Fig. 1, *C-V* curves measured at 300 kHz are presented. This frequency can be considered high enough that the interface states cannot respond to it. The shape of the curves for plasma-treated Si shows variations typical of a high density of interface traps. Further measurements taken in descending order of frequency reveal *C-V* curves stable in shape and position. In these measurements, the first trace indicated a hysteresis effect, which was followed by stabilization under further measurements. This effect is most obvious for oxides prepared on plasma hydrogenated Si, without heating. The hysteresis is related to border traps, i.e. near-interfacial oxide traps that can either rapidly or slowly exchange charge with the silicon. The first measurement trace at 300 kHz reveals the virgin *C-V* curve before the border traps have been filled. Thus, this curve shows the real density of interface traps, i.e. the traps that are located sharply at the interface, while the border traps are located deeper in the interface region.

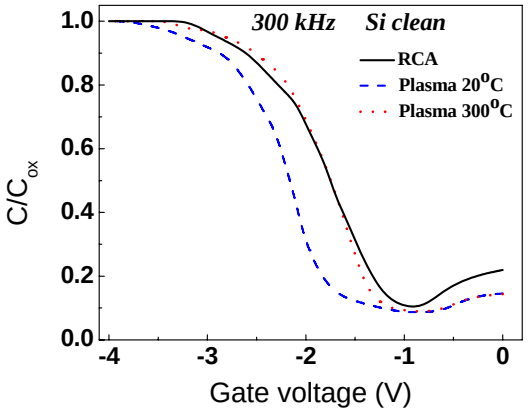

Fig. 1. C-V curves of the MOS capacitors.

Some of the border traps are being filled during this first trace, when the structure was negatively biased, and this contributes further as fixed oxide charge. This is seen as an increased oxide charge by the next measurements at descending frequencies. The other fraction of the border traps become active only after the negative biasing after the first trace, and then act as interface traps. This results in a reduced slope of the subsequently measured *C-V* curves.

The *C-V* curve for Si not heated during plasma hydrogenation shifts to more negative voltages, indicating a higher density of oxide traps. This curve exhibits the highest slope, higher even than that for RCA Si, showing the lowest density of interface traps. This is somewhat surprising, since exposure to RF plasma of the Si before oxidation is expected to generate radiation defects [6]. The *C-V* curve of the 300°C sample is also steeper in comparison to the RCA curve, which indicates an overall lower density of traps, which can be attributed to an annealing or passivation effect. The oxide defect densities, as obtained from flatband voltages V_{fb}, are given in Table 1.

Table 1. Defect density concentrations: flatband fixed oxide charge Q_{fb}, border traps N_{st} and intrinsic oxide charge Q_{if} for oxides with different pre-oxidation conditions.

Si wafer pre-oxidation clean	Q_{fb} (cm^{-2})	N_{st} (cm^{-2})	Q_{if} (cm^{-2})
RCA	$1.7x10^{12}$	$3.3x10^{11}$	$5.1x10^{11}$
Plasma: unheated	$2.0x10^{12}$	$11.0x10^{11}$	$-1.2x10^{12}$
Plasma: 300°C	$1.6x10^{12}$	$5.3x10^{11}$	$6.1x10^{11}$

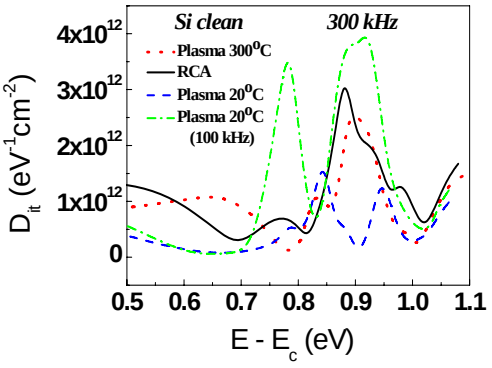

Fig. 2. Interface trap profiles in the Si bandgap.

The interface traps density distributions D_{it} obtained from the 300 kHz *C-V* characteristics are shown in Fig. 2. On the same figure, the D_{it} profile from the 100 kHz *C-V* curve for the unheated sample is shown. It illustrates the interference of the border traps, as discussed above. The interface trap distributions exhibit localized states in the lower part of the Si bandgap. The densities around midgap are below 10^{12} $eV^{-1}cm^{-2}$ for the plasma exposed wafers, which is even below the value of $1.3x10^{12}$ $eV^{-1}cm^{-2}$ for the RCA sample. It is known that the dangling Si bonds form a peak at 0.3 eV above the valence band edge E_v [7]. The peak about this position is seen also in our oxides, with exception of the oxide on Si hydrogenated at 300°C, which indicates an annealing effect. In this oxide a broad peak appears at 0.45 eV above E_v, also related to dangling Si bonds. Often the dangling bonds have been identified as the so called P_b centres. The levels at 0.3 and at 0.45 eV above E_v are attributed to P_{bo} and P_{b1} centres in (100)Si, respectively [8].

Generation of P_b defects is related to intrinsic interface stress of Si/SiO_2 [9]. For our oxides, the stress levels as obtained by ellipsometric measurement [10] are $4.0x10^8$ N/m^2 in RCA oxides and lower in oxides on unheated Si, having a value of $3.1x10^8$ N/m^2 which is in accordance with the densities of the 0.78 eV (0.3 above E_v) peak in Fig. 2. The double peak around 0.9 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 [11]. However, such a defect complex can be expected even in non-irradiated oxides, being a result of the oxidation process. These defects are due to not fully oxidized Si in the interface region. Here, this is seen from the peak in the D_{it} distribution for the RCA oxide, which has not received any annealing. For the oxide on unheated Si at 300 kHz in Fig. 2, this peak clearly splits into two states as seen, caused by plasma exposure of Si surface during hydrogenation. The same splitting of the peak is observed for the 100 kHz *C-V* curve. The interface trap profile for the oxide on unheated Si at 300 kHz shows a significantly lower density over the whole measured energy interval, as compared to the 100 kHz *C-V* curve profile. This distribution is of special importance, since it enables one to get some estimate of the real energy profile of the interface traps.

A good correlation with the *C-V* results was found from examination of the *G-V* characteristics. Detailed information on the frequency dispersion of both the *C-V* and *G-V* curves can be found in [12].

Here, only the *G-V* curves at 100 kHz are displayed, in Fig. 3. The positions of the peaks at

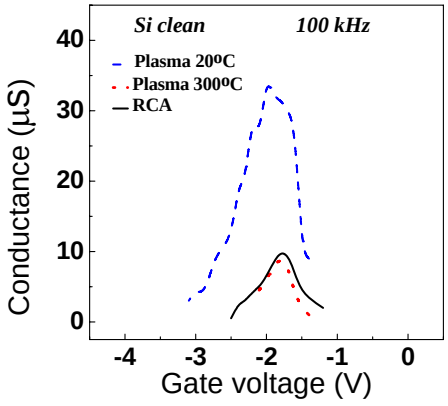

Fig. 3. G-V curves of the MOS capacitors.

different gate voltages correspond to the positions of the peaks in Fig. 2. Also, the highest interface trap density was found for oxides on unheated Si, manifested by the highest *G-V* peak. The complicated shape of the *G-V* curves indicates a superposition of peaks, related to different trapping states.

The frequency dispersion of the flatband voltages V_{fb} can yield further information on the oxide charges. This is seen in Fig. 4, where plots of V_{fb} versus log*f* are given. All V_{fb} values lie on a straight line, except for the values of V_{fb} at 300 kHz which are shifted in the positive direction. The reason is that the *C-V* measurement was started at this frequency, and at successive frequencies the border traps were already filled with carriers. Therefore, the density of the border traps N_{st} was estimated from the difference between the 300 and 200 kHz points.

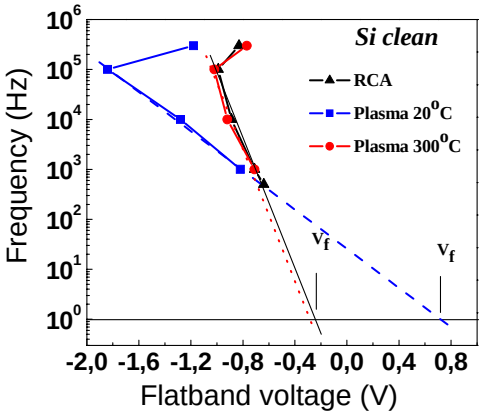

Fig. 4. Frequency dependence of V_{fb} shifts.

The slopes of the straight lines have the same sign, which can be attributed to the same type of border traps - donor type. The higher frequency dispersion for oxides on unheated Si should be related to a higher N_{st}. This is reasonable, since the higher density N_{st} can be regarded as plasma induced radiation defects, additional to the defects generated by the oxidation process. It can be seen that in 300°C oxides, N_{st} decreases as compared to the unheated samples, due to the suppression of radiation defect generation by the higher substrate temperature during plasma treatment. The densities of the oxide defects are summarized in Table 1.

The interface trap contribution to the V_{fb} value can be significantly reduced if an extrapolation to low frequencies of the V_{fb} values is made [5]. The obtained charge density will be referred as intrinsic oxide charge Q_{if}. Here Q_{if} are estimated from V_{fb} vs. log f plots in Fig. 4, extrapolating the lines to the 1 Hz level.

Obviously, RCA and 300°C oxides revealed positive Q_{if} charges typical for thermal oxides, while plasma treatment without heating resulted in the generation of negatively charged oxide defects most probably due to capture of electrons in the border traps. The role of the temperature during Si hydrogenation on the built-in charges in the oxide is evident.

5. Conclusions

Frequency *C-V* and *G-V* analysis demonstrated the generation of localized interface traps due to dangling Si bonds, O/V complex defects and border interface traps. The intrinsic oxide charge revealed the generation of negative charges in oxides grown on Si, hydrogenated without heating. 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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