JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 2, February 2007, p. 398 - 401

Electrically active defect centers in MOS structures with nanosized SiO_2 thermally grown on plasma hydrogenated silicon

S. ALEXANDROVA[a*], A. SZEKERES, E. VALCHEVA[b], E. VLAIKOVA
Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria.
[a] *Department of Applied Physics, Technical University, 8 Kl. Ohridski Blvd., 1797 Sofia, Bulgaria*
[b]*Department of Solid State Physics and Microelectronics, Sofia University, 1164 Sofia, Bulgaria*

This paper presents results on the characterization of the electrically active interface defect centers in Si/SiO_2 structures formed on Si wafers exposed to a rf hydrogen plasma. The aim is to achieve hydrogenation of the Si near-surface and, possibly, a low defect concentration due to hydrogen termination of unsaturated bonds. During plasma treatment the Si wafers could be heated up to 300°C. The 9 nm SiO_2 layer was formed by thermal oxidation at a reduced temperature of 850°C, according to the contemporary requirements of the technology. For investigations, multiple frequency *C-V* and *G-V* measurement techniques were applied. The presence of single defects with different energy levels in the Si bandgap was established in oxides on plasma cleaned Si. The role of the Si substrate hydrogenation is to bring about a more ordered interface region.

(Received November 1, 2006; accepted December 21, 2006)

Keywords: MOS structures, Hydrogenation, Hydrogen plasma, Oxidation, Electrical characteristics

1. Introduction

The key structure in the Si-based electronic industry in the last 35 years was Si and its thermal oxide. This is perhaps the most perfect combination between two solids, with small leakage through the oxide and very few defects in the interface region formed by the transition from the crystalline silicon lattice to the amorphous SiO_2 network. The concentrations of these defect centers determine the electrical functioning of the devices. However, now, as a result of the latest miniaturization of electronic devices the oxide thickness lies in the nanometre range. Gate dielectric bottlenecks are limiting circuit speeds and new materials are being introduced into microelectronics manufacture, and alternative technologies are also being considered [1]. As our recent studies have shown [2] that plasma hydrogenation of the Si wafer prior to thermal oxidation can offer several advantages, such as low interface defect concentrations and decreased mechanical oxide stress, achieved by suitable oxidation rates and oxidation temperatures.

This paper presents results on the characterization of the electrically active interface defect centers in Si/SiO_2 structures formed on Si wafers exposed to a rf hydrogen plasma. The aim is to achieve hydrogenation of the Si near-surface and, possibly, a low defect concentration due to hydrogen termination of unsaturated bonds by introducing H species into the oxide during its growth. A correlation with the results from optical measurements, such as the refractive index and mechanical stress is discussed. Note that the studies have been performed on structures without any thermal post-oxidation treatments, and hence have the advantage that (i) conclusions can be made about the nature of the as-grown defect centers and (ii) the possibility exists of achieving good quality oxides without any additional high temperature annealing, by relying on the beneficial effect of the hydrogenation of the Si substrate.

2. Experimental

The structures used in this study were MOS capacitors formed on 5-10 Ohm.cm *n*-type (111)-oriented single-crystal Si wafers. The Si substrates were cleaned using a standard RCA procedure (H_2SO_4/H_2O_2 solution followed by a dip in diluted HF and a rinse in deionized H_2O). Some of the samples were subsequently exposed to a rf hydrogen plasma in a planar plasma unit. The rf (13.56 MHz) generator was capacitively coupled to the reactive chamber with an input power of 15 W. The gas pressure was 133 Pa. The substrates were kept on the lower electrode without heating (for simplicity referred to below as 20°C), or at a temperature of 300°C for 15 min. The aim of this procedure was to hydrogenate the Si near-surface region to alter the oxidation kinetics and, possibly, to achieve better electrical properties of the resultant MOS structures. The oxidation of the Si wafers was performed in dry O_2 ambient at 850 °C in the same oxidation run for all substrates, RCA cleaned and plasma exposed. The RCA cleaned samples with only served for comparison, for revealing the possible advantages of the plasma cleaning technology.

Using a high precision spectral Rudolf Research ellipsometer, information on the properties of the oxide and the interface region between the Si and SiO_2 was gained. From detailed measurements in the visible range the thickness and refractive index of the SiO_2 layers were obtained, as well as the composition and width of the interface region. The mechanical stress across the oxide was estimated from the dielectric function analysis.

The MOS capacitors were formed by vacuum evaporation of Al dots. As a contact to the silicon backside, a continuous Al film was evaporated. Information about the concentrations of the electrically active defects was obtained by analysis of the frequency dispersion of the capacitance-voltage (*C-V*) and the conductance-voltage (*G-V*) characteristics of the MOS structures. Room temperature *C-V* and *G-V* measurements were performed in the frequency range 1 kHz to 300 kHz. The measurement unit was a Precision Component Analyzer WAYNE KERR 6425. The fixed oxide charge density (Q_{ox}) and the interface trap density (D_{it}) were evaluated by comparison of the experimental and ideal theoretical *C-V* characteristics. Additionally, information on the interface trap density was obtained from the *G-V* measurements.

3. Results and discussion

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. The thickness of the SiO_2 layers 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 [2]. 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 [3]. The refractive indices were higher than 1.46, the value typical for stress free oxide.

Table 1. Basic oxide parameters of the samples.

Si surface clean	T_{ox} [nm]	n	Stress [10^8 N/cm^2]	T_{int} [nm]
RCA and dry H_2 plasma, 20°C	10.3	1.489	5.1	0.98
RCA and dry H_2 plasma, 300°C	9.8	1.478	5.3	0.6
RCA clean only	9.0	1.496	6.3	1.0

The dielectric function ε, calculated from the refractive index dispersion curves, allows estimation of the stress level from the shift of the peak position in the region 3.1-3.7 eV, the procedure for which is published in [4]. Obviously, the oxidation process of the hydrogenated Si is related to lower build-in stress, as is evident from Table 1. This can be understood, as we have previously suggested, by the formation of a top layer on the Si surface containing voids. This has the implication of a less dense and, consequently less stressed structure at the Si/SiO_2 interface. The most interesting point here is that the less stressed oxide (H_2 plasma at 20°C cleaning) is not related to the thinnest optical interface region but to the roughness level, as obtained by Atomic force Microscopy (AFM) studies [5]. It does not obviously coincide with the part of the interfacial region where the electrically active defects are localized. It can be expected that the stress and interface width should to be directly related to the defects in this region, which can show up in the electrical characteristics, such as the *C-V* and *G-V* curves. However, any electrically inactive defects can still contribute to the stress level but cannot be detected in these characteristics.

The role of the plasma pre-oxidation treatment on the electrically active interface defects is illustrated in Figs. 1 and 2, for MOS structures with oxides grown on plasma exposed substrates without heating or heated at 300°C, respectively.

In these figures, frequency dispersion is evident the one for the MOS structure with Si treated in plasma at 20°C being less pronounced.

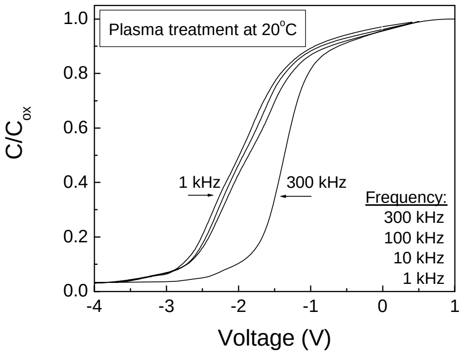

Fig.1 Frequency dispersion of the C-V curves for MOS structures on Si cleaned in plasma at 20°C.

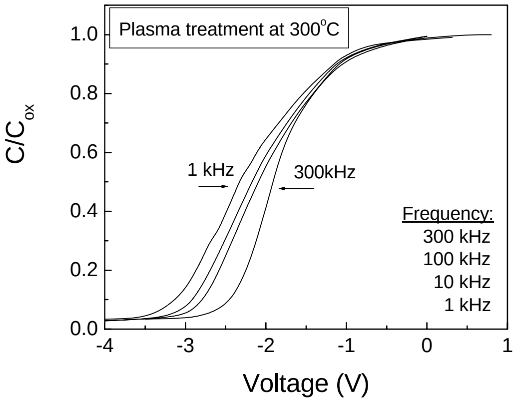

Fig.2 Frequency dispersion of the C-V curves for MOS structures on Si cleaned in plasma at 300 °C.

The MOS structures formed on RCA cleaned Si substrates exhibit frequency dispersion, which is similar to those on 300°C plasma cleaned Si (Fig. 2). It should be mentioned that the careful analysis of the *C-V* curves has shown that the MOS structures with a SiO_2 layer grown on plasma treated Si without heating exhibit a slight hysteresis in the measured curves (less than 0.2 V at the flatband condition in the voltage sweep range of -5V to 5V), indicating the presence of traps near the interface, spatially distributed into the oxide (border traps). The oxide leakage currents were negligible small. Only in the case of MOS structures with the oxide grown on unheated Si substrates was there a slightly increased leakage above $5x10^8$ V/cm, which still didn't hinder the measurement. These findings imply high-quality dielectric layers. As concerns the interface region, from the *C-V* curves it can be concluded that the shifts along the voltage axis for both plasma oxides reveal an oxide charge of the order of 10^{12} cm^{-3} ($2.8x10^{12}$, for oxides on hydrogenated Si and $4.3x10^{12}$ cm^{-3} for oxide on RCA cleaned Si, respectively). These values are relatively small for unannealed oxides [6].

Analyzing the shape of the curves, one can get quite a clear picture of the interface traps in the structures. For this reason, and also for comparative purposes, the 300 kHz C-V curves for all three kinds of oxides are plotted in Fig. 3.

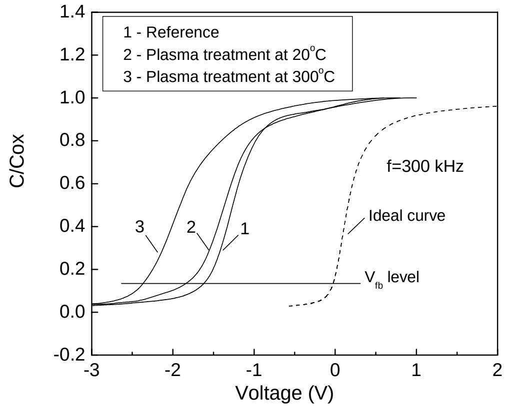

Fig. 3. High frequency C-V curves for MOS structures on Si cleaned at different conditions.

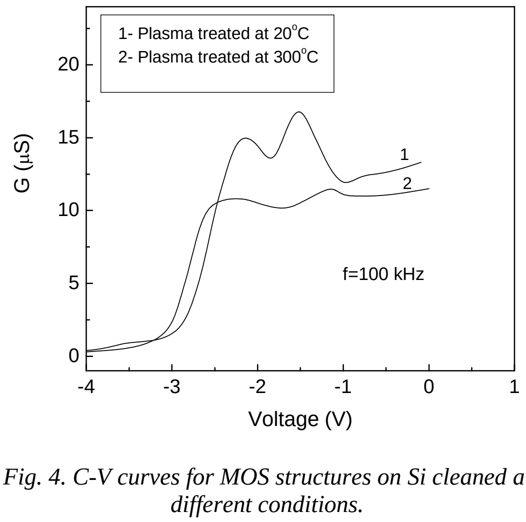

Fig. 4. C-V curves for MOS structures on Si cleaned at different conditions.

From the experimental *C-V* curves and the ideal curve, it can be seen that the oxides grown on plasma cleaned Si show higher curve slopes, which is usually attributed to an increased overall interface trap density. The curve for the oxides grown on RCA cleaned Si, in spite of the lower slope around the flatband condition, reveals a special feature when approaching accumulation possibly indicating a peaked structure in the interface trap density spectrum. The oxides grown on 20°C plasma treated Si exhibit an increased density in depletion. Such effects are not observed in the case of oxides grown on Si heated to 300 °C during plasma exposure. Most probably, at 300°C certain interface precursor defects are annealed. Similar conclusions can be drawn from the *G-V* curves displayed in Fig. 4. Both the *C-V* and *G-V* characteristics indicate the presence of interface traps with at least two localized energy levels in the Si bandgap. Peaked structures in the interface densities are evident, which are more clearly seen in the 20°C plasma oxides (Fig. 4).

These observations can be clearly seen in Fig.5, where the interface trap density spectra gained from the *C-V* curves in Fig.3 are plotted. The most pronounced peaked features in the depletion and weak accumulation regime for the oxides grown on plasma cleaned Si are evident the density for the 300°C oxide being smaller due to the cited annealing effect. The highest density revealed in the RCA oxides is seen as a broad maximum. Approaching accumulation possible peaks, as inferred from the curves in Figs. 3 and 4, cannot be discerned, because of the increasing influence of the method inaccuracy in this energy region of the Si bandgap. Peaks in the density distribution in the upper part of the band gap are usually related to the presence of weak Si-O bonds and weak Si-O interactions [7].

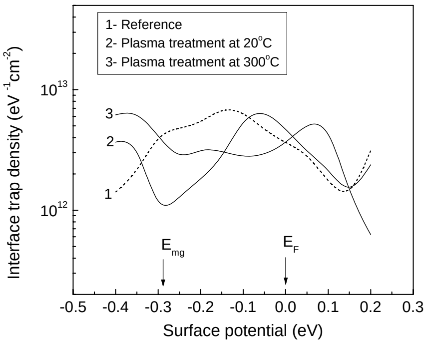

Fig. 5 Interface trap density distribution over the Si bandgap for MOS structures formed on Si cleaned under different conditions.

These defect sites can be expected to correlate with the interface width and the stress level given in Table 1. In Fig.5 these peaks reveal a smaller density (regarded as a peak density and integral density below the peak) for oxides on plasma cleaned Si, the density being smaller for 300 °C oxides. The broad structured peak (possibly triple superimposed) centered at –0.15 eV, with the highest concentration of weak Si-O bonds in RCA oxides, correlates well with the highest oxide stress and refractive index (Table 1). Further correlation is observed with the increased density near -0.4 eV. Peaks in this energy range are usually attributed to Si dangling bonds [7]. In this energy region, the oxides on RCA cleaned Si show the least concentration, which relates to the more compressed interface region. In the oxide on plasma cleaned Si, this interface region is less dense because of the modified surface Si layer, where the voids are the origin of dangling Si bonds left after hydrogen release during oxidation. Most probably the role of the hydrogenation of the Si substrate is, along with enhancement of the oxidation rate [2], to bring about a more ordered interface region. This is also in good agreement with the values of the refractive index in Table 1, as well as with the Si-O-Si angle distribution obtained from IR studies [8], where it has been found that this distribution is much broader for the RCA oxides showing less ordered interface structures. The structure is characterized by more 4-rings of SiO_2, in contrast to oxides on plasma cleaned Si, where the energetically favorable 6-rings structure is prevalent.

In comparison to the thicker oxides (~ 13 nm) grown under the same technological conditions [8], the overall concentrations of the defect centers in 9 nm oxides show slightly lower values and different detailed shape of the distributions. The flatter profiles in the 13 nm oxides are partially due to the longer period at the oxidation temperature. This results in annealing of the plasma-induced precursors and release of the oxide stress.

4. Conclusions

Electrically active defect centers in 9 nm SiO_2 oxides, grown on plasma cleaned Si, have been studied. From *C-V* and *G-V* measurements, a clear indication is found for the presence of single defects with different energy levels in the Si bandgap, in oxides on plasma cleaned Si. These observations are well correlated with the results on the oxide mechanical stress level, oxide composition and ring structure, as well as with the composition and thickness of the interfacial region. The role of the hydrogenation of the Si substrate is to yield a more ordered interface region.

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[*] Corresponding author: salex@issp.bas.bg