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Reliability degradation of thin HfO_2/SiO_2 gate stacks by remote RF hydrogen and deuterium plasma treatment

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ABSTRACT

Current–voltage measurements indicated that RF hydrogen/deuterium remote plasma treatment of thin p-Si/SiO_2/HfO_2 structures proved to be detrimental in terms of dielectric reliability. By using capacitance–voltage measurements we demonstrate that this reported degradation was not attributed to plasma-induced defects but rather due to an enhanced liberation of hydrogen and deuterium species during the electrical stress.
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1. Introduction

It is well known that hydrogen influences many electrophysical properties of Si/SiO_2 structures [1]. However, as SiO_2 is bound to be replaced at the next stage of scaling by high *k* dielectrics, most probably by HfO_2 or one of its silicates, it is very important to determine how the incorporation of hydrogen will affect the electrical properties of these novel oxides. Although much work has been devoted to establishing the effects of a standard forming gas annealing on the electrical properties of SiO_2/HfO_2 gate stacks, [2,3], and some previous work has been published on the effects of RF hydrogen plasma on Si/SiO_2 structures,[4], to the best of our knowledge very little work has been previously reported on the effects of a hydrogen plasma treatment on the electrical behavior of such novel dielectrics. This is important as plasma processing is used extensively in silicon technologies. The objective of this work is to demonstrate the effects of remote hydrogen and deuterium radio frequency (RF) plasma treatment of a SiO_2/HfO_2 gate stack in terms of dielectric reliability.

2. Experimental

The samples under study (p-Si/SiO_2/HfO_2) were fabricated at IMEC and consisted of a 4 nm HfO_2 grown by MOCVD on a 1 nm chemically grown interfacial SiO_2 layer. The plasma system consisted of a quartz tube through which a molecular hydrogen/deuterium gas at 1 mbar was pumped. The hydrogen plasma was excited by a 13.56 MHz RF generator connected to a copper coil encircling the tube. Samples were placed in a remote position in respect to the copper coil, approximately 10–20 cm downstream from the plasma itself (remote plasma treatment). Plasma treatments were carried out on bare oxide surfaces prior to metallization, at room temperature. Following the plasma treatment, MOS capacitors were formed by vacuum thermal evaporation of Au (1 mm circular gate dots). Electrical characterization was performed by means of an Agilent 4156C semiconductor parameter analyzer and a HP 4192A impedance analyzer.

3. Results and discussion

In Fig. 1 we illustrate gate current vs voltage characteristics of a 1 nm SiO_2/4 nm HfO_2 gate stack before (control samples) and after hydrogen, deuterium and oxygen plasma treatment.

From Fig. 1 it is evident that structures which underwent hydrogen plasma treatment exhibited a considerable increase in the leakage current (approximately 3 orders of magnitude) and a reduction in the breakdown voltage (V_{BD}) as compared to control samples which had not been exposed to plasma. Devices that underwent deuterium plasma treatment also seem to be degraded compared to control samples however to a considerably less extent than the hydrogen treated ones. Also from Fig. 1 we observe that in contrast to the hydrogen–deuterium treatment, oxygen plasma exposure did not have such a pronounced degradation effect in the reliability of the gate stack under test apart from a small reduction in the breakdown voltage as compared to control devices.

A key question was to determine the source of the degradation of the oxides and explain why hydrogen/deuterium plasma treated structures exhibited such deterioration in terms of dielectric reliability. A possible explanation could be that the stack was etched during the plasma

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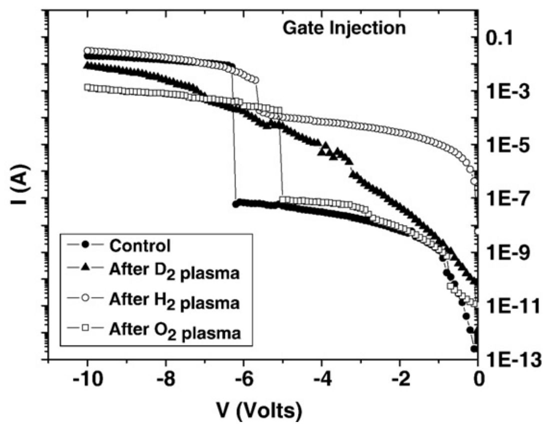

Fig. 1. *I–V* characteristics (gate injection) of a 1 nm SiO_2 4 nm HfO_2 gate stack for control devices and devices after H_2, D_2 and O_2 plasma treatment. Plasma treatments were carried out at 50 W for 1 h.

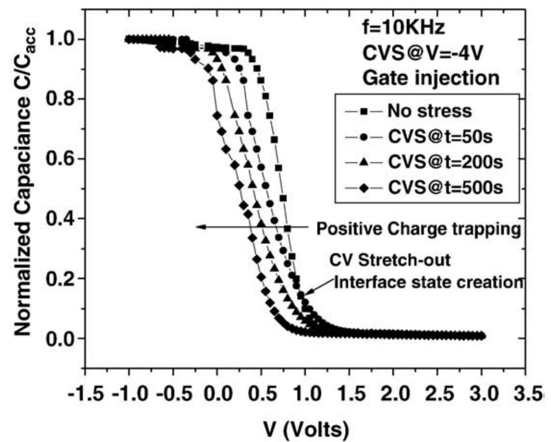

Fig. 3. High frequency capacitance–voltage characteristics of a hydrogen plasma treated 1 nm SiO_2/4 nm HfO_2 gate stack measured before and after constant voltage stress at $V=-4$ V.

treatment and that the degradation was simply due to oxide thinning (thinner oxide, larger tunneling current) however by monitoring the thickness (electrically via the high frequency capacitance in accumulation) of the stack before and after the plasma exposures, no change in the thickness was observed. Also one might argue that the plasma treatment was responsible for creating electrically active defects in the oxide as was previously reported by Simeonov and co workers [5], and that trap-assisted tunneling through these defects was the cause of the degradation. However if degradation was mainly related to plasma damage one would expect that O_2 plasma treatment would induce the largest degree of damage compared to H_2/D_2 treatment due to the much larger mass of oxygen ions.

Next we provide experimental evidence to support the idea that during electrical stress hydrogen species are liberated which are responsible for the oxide degradation as described by the hydrogen release (HR) model [6]. We believe that the enhanced degradation after H_2 plasma treatment is due to the excess amount of hydrogen incorporated in our samples during the course of the plasma exposure, this is liberated in the course of the subsequent stress giving rise to additional damage. In Fig. 2 the relative capacitance at inversion $[C_{inv}(t)-C_{inv}(0)]/C_{inv}(0)$ of our structures is plotted as a function of time during a constant voltage stress at $V=-4$ V.

From Fig. 2 it is evident that the inversion capacitance decreases with stress time. This decrease indicates the release of hydrogen species during the stress which diffuse in the p-Si substrate, resulting in the deactivation of boron acceptors through the formation of neutral

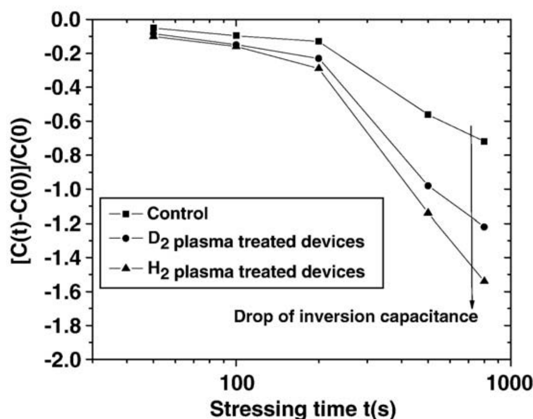

Fig. 2. *I–V* normalized variation of the inversion capacitance of a 1 nm SiO_2 4 nm HfO_2 gate stack as a function of the stress time during a constant voltage stress of $V=-4$ V (gate injection). Results are illustrated for control and H_2 and D_2 treated devices.

B–H complexes [7]. Also from Fig. 2 it is evident that the drop in the inversion capacitance is much more prominent for H_2/D_2 treated devices which indicates that much more hydrogen is released during the stress of plasma treated devices in respect to control structures.

Next in Fig. 3 we illustrate *C–V* characteristics of a hydrogen treated device before and after constant voltage stress of $V=-4$ V.

From Fig. 3 it is evident that constant voltage stress results in trapping positive charge (parallel shift of the *C–V* curve to negative voltages) and in interface defect generation (CV stretch-out) which can be correlated to hydrogen release during stress as follows: During the electrical stress electrons injected from the gate arrive at the Si/SiO_2 interface and the electron impact results in the de-passivation of $Si_3\equiv SiH$ centers and the subsequent formation of $Si_3\equiv Si$-dangling bonds, the so called Pb centers [8]. Having been liberated hydrogen is transported through the dielectric by the oxide's electric field where it may result in the creation of positively charged centers either in the SiO_2 layer or in the HfO_2 bulk or in the generation of hydrogen-induced neutral traps [9].

4. Conclusions

Remote hydrogen plasma treatment is detrimental in relation to the dielectric reliability of SiO_2/HfO_2 gate stacks during electrical stress. We believe that this damage was not caused by plasma-induced electrical defects but due to the fact that during the plasma exposure a large amount of hydrogen was incorporated into the oxide. Upon electrical stressing this hydrogen was liberated causing an "enhanced" degradation effect. Hydrogen release during stress was shown to occur by employing capacitive–voltage measurements.

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