A study of chemical ultra thin silicon oxide films by FTIR-ATR and ARXPS after wet cleaning processes.

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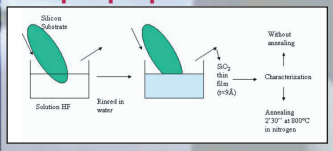
Introduction

The development of advanced CMOS devices will require a gate dielectric thickness in the order of 0.5 to 1 nm (equivalent oxide thickness EOT) in order to control the gate capacitance, and the drive current capability of CMOS transistors. The gate capacitance control will be achieved by introducing high k to materials instead of conventional thermal on silicon oxide. Most of the investigated high k materials (HfO_2 , ZrO_2 ; Hf and Zr silicates, lanthamide oxides,…) are not really compatible with Si. They exhibit a tendency to react with crystalline Si and to form an interfacial layer, generally composed in a mixture of the high k layer and SiO_2. In order to prevent the growth of any uncontrolled interfacial layer between the high k layer and silicon substrate, an ultra thin SiO_2 layer is prepared using chemical and/or thermal techniques. The chemical composition of this chemical SiO_2 layer, which has been prepared using RCA, RHO_3 and DDC, has been investigated using ARXPS and ATR-FTIR.

Sample preparation



Solution
RCA=SC1(65°C) + Rinse (50°C) + SC2 (65°C) +Rinse (50°C)
SC1 = (NH_4OH/H_2O_2/DIW)
SC2 (HCl/H_2O_2/DIW)
DDC = 6ppm O3/0.01%HCl
RHO_3 Standard RCA + diluted HF+ 6ppm O_3/0.01%HCl

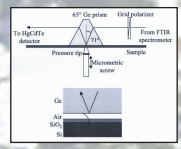
EXPERIMENTAL

S.Probe Surface Spectrometer System

- Al Kα-Xray source
- Hemispherical analyser
- Angle-Resolved X-ray Photoemission Spectroscopy (ARXPS)
- FWHM = 0.73eV with a spot size of 250x1000μm^2 (Au (4f72))

ATR-FTIR

Attenuated Total Reflection Fournier Transform Infra-Red
FTIR Bruker IFS 55

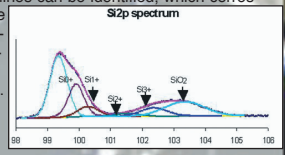


Spectral region : 600-4500cm^{-1}

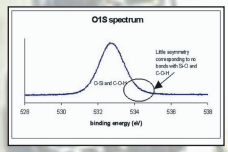
RESULTS

ARXPS

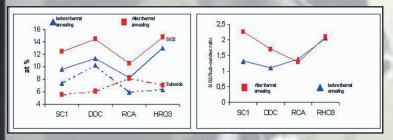
- Si2p core level spectrum : three peaks between the Si and the SiO_2 lines can be identified, which correspond to the three possible sub-oxide states, usually denoted Si^{1+}, Si^{2+}, Si^{3+}.



- O1s peak is simulated with one component attributed to both Si-O and C-O-H bonds. Nevertheless, an asymmetry of the peak at high binding energy is sometimes observed. This state could be attributed to physi- or chemisorbed oxygen.



Atomic concentrations of SiO_2 and sub-oxides. SiO_2 and sub-oxides ratio as a function of the silicon oxides.



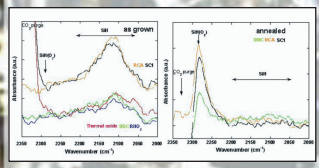
After thermal annealing

SC1 and DDC
tendency to form SiO_2
- SiO_2 component increases.
- sub-oxide species components decrease

RCA and RHO_3
- the rearrangement is into sub-oxide lattice.

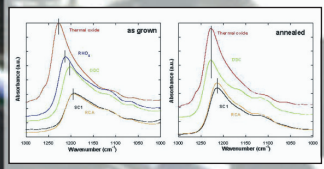
Si-H region

- More Si-H bonds for RCA and SC1 than for DDC and RHO_3 before annealing
- Apparition of $SiH(O_3)$ bond and disparition of SiH bond with annealing for all oxides



Si-O-Si region

- RHO_3 and DDC oxydes are more «thermal like» than SC1 and RCA before annealing
- Annealing increase the order in the oxide layer, but DDC and RHO_3 are always more «thermal like» than SC1 and RCA



Discussion

Summary of results is obtained in this study by FTIR-ATR and ARXPS
- (-) Less organization =>(+) => (++)=>(+++) more organization (Terms of stress, voids, sub-oxides and roughness)
- SiO_2 -: tends toward SiO_2
- Interface: the rearrangement is into sub-oxide

FTIR-ATR	RCA	SCI	RHO_3	DDC	ARXPS	RCA SCI RHO_3 DDC
Before thermal annealing	(-)	(-)	(+)	(+)	Before thermal annealing	All the oxides present have nearly the same chemical structure
After thermal annealing	(++)		(+++)	(+++)	After thermal annealing	Interface SiO_2

Conclusion

After thermal annealing of chemical oxides, ARXPS and FTIR-ATR results shows reorganization of the interface or of the volume of all oxides. Two kinds of rearrangement have been detected, a rearrangement of the whole oxide layer, or a growth of the silicon oxide at the interface. ARXPS measurements show their ability to characterize interfaces compounds. FTIR-ATR measurements give a detailed investigation of the whole layer chemical structure.
The proof has been made of the utility of using both of these two techniques in order to have a whole characterization of layers properties (interface and thickness).