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 (HfO₂, ZrO₂; Hf and Zr silicates, lanthanide 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 SiO₂. In order to prevent the growth of any uncontrolled interfacial layer between the high k layer and silicon substrate, an ultra thin SiO₂ layer is prepared using chemical and/or thermal techniques. The chemical composition of this chemical SiO₂ layer, which has been prepared using RCA, RHO, 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 = (NH₄OH/H₂O₂/DIW)
SC2 = (HCl/H₂O₂/DIW)
DDC = 6ppm O₃/0.01%HCl
RHO₃ Standard RCA + diluted HF+ 6ppm O₃/0.01%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 250x1000µm² (Au (4f7/2)

RESULTS

Si-H region
• More Si-H bonds for RCA and SC1 than for DDC and RHO₃ before annealing
• Apparition of SiH(OH) bond and disappearance of SiH bond with annealing for all oxides

Si-O-Si region
• RHO₃ and DDC oxides are more «thermal like» than SC1 and RCA before annealing
• Annealing increase the order in the oxide layer, but DDC and RHO₃ 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)
• SiO₂ «-» tends toward SiO₂
• Interface: the rearrangement is into sub-oxide

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).