Investigation of the Electronic Properties of the ZrO_2 and HfO_2 Thin Films by Scanning Probe Microscopy and X-ray Photoelectron Spectroscopy

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ABSTRACT

In this paper the results of SPM and XPS investigation of HfO_2 (4,7 nm) and ZrO_2 (24 nm) films grown by Atomic Lay Deposition (ALD) are presented. The effect of annealing of the HfO_2 and ZrO_2 films grown by ALD on their electronic properties has been studied by combined AFM/STM. Investigation of the dependence of the morphology and conductivity of the thin high-k insulator films on the annealing temperature reveals some important details of the degradation kinetic of such layers in contact with Si.

Keywords: high-k gate insulators, silicides, combined AFM/STM, ZrO_2, HfO_2.

1 INTRODUCTION

Investigations of the dielectric materials promising for application as gate insulators in the advanced Metal-Oxide-Semiconductor Field Effect Transistors (MOSFETs) with the thickness of the gate dielectric ~ 1 nm has recently got renewed interest [1,2]]. HfO_2 and ZrO_2 are the most promising candidates for application as the gate insulators among the metal oxides.

It is well known [3,4,5] that the ultra thin HfO_2 and ZrO_2 layers grown on Si are instable with respect to annealing under usual conditions in semiconductor device processing, especially in UHV, and degrade with formation of the respective silicides. However, the exact mechanism of oxide degradation at the interface with Si is still debated.

In this work the results of Scanning Probe Microscopy (SPM) and X-ray photoelectron spectroscopy (XPS) investigation of HfO_2 (4.7 nm) and ZrO_2 (24 nm) films grown by Atomic Lay Deposition (ALD) are presented. Influence of annealing of the HfO_2 and ZrO_2 films grown by ALD on their electronic properties has been studied by combined Atomic Force / Scanning Tunneling Microscopy (combined AFM/STM).

2 COMBINED AFM/STM TECHNIQUE

In combined AFM/STM measurements we used a standard beam deflection AFM with a conductive cantilever. The feedback was maintained by AFM technique in the contact mode. I-V curves of the tunneling contact between the cantilever and p+-Si substrate through the dielectric film were recorded simultaneously in every point of the scan. This approach allowed us to decouple maintaining the feedback and measuring the tunneling current, and thus to study the electronic properties of the partial tunneling opacity insulator layers.

3 EXPERIMENT DETAILS

The combined AFM\STM experiments were carried out using Omicron UHV AFM/STM LF1. The silicon cantilevers covered with platinum were used. The radius of the probe apex was ~ 50 nm.

The ZrO_2 (24 nm thick) and HfO_2 (4.7 nm thick) films deposited on a p^+-Si by Atomic Layer Deposition (ALD) in MDM-INFM Laboratory (Italy) was used.

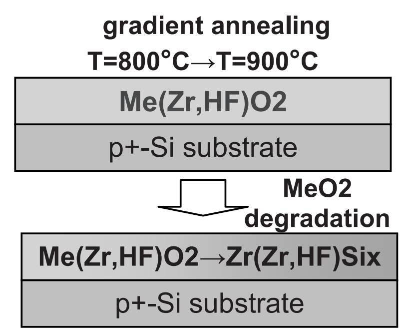

Figure 1: Schematic drawing of the samples.

To investigate the degradation kinetics, the ZrO_2/Si and HfO_2/Si samples were annealed in UHV with the temperature gradient across the samples in the range of T = 800-900^{0}C as measured with a pyrometer. *In situ* X-ray Photoelectron Spectroscopy (XPS) measurements in different areas on the sample surface revealed complete conversion of ZrO_2 into Zr silicide at T=900^{0}C, while no sign of silicide formation was seen on the opposite end of the sample (T=800^{0}C).

4 RESULTS AND DISCUSION

In Figure 2 the morphology and the current images of HfO_2 film (4.7 nm) annealed in vacuum to a full degradation are shown. The small islands (grains) of silicide in the area of full degradation of the oxide have been observed.

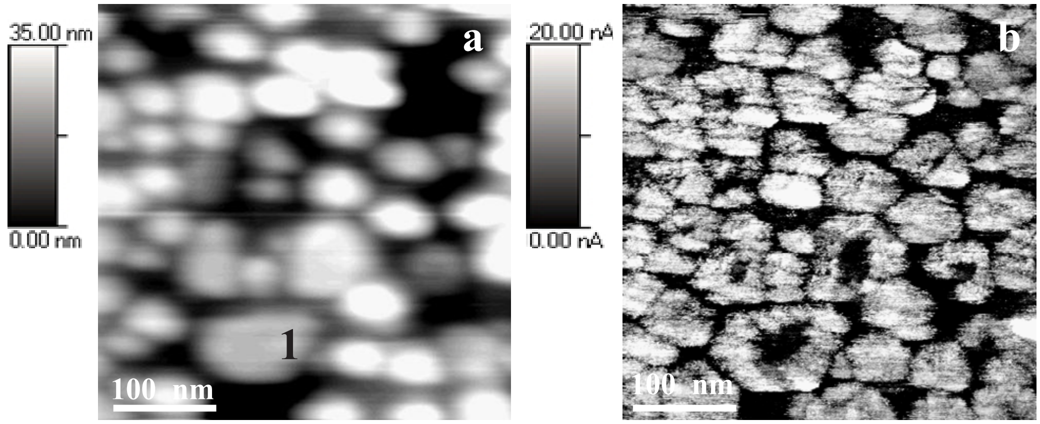

Figure 2: Morphology (a) and current image (b) of HfO_2 film after vacuum annealing at T ≈900 °C.

The height of the grains varied from 15 up to 40 nm; the diameter – from 30 up to 90 nm. The correlation between the morphology and the current image was observed.

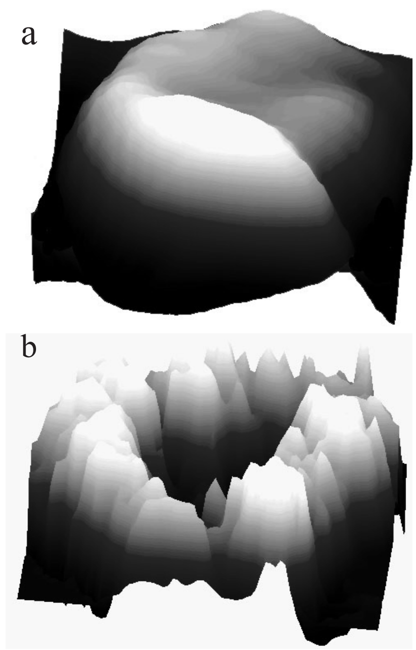

Figure 3: Morphology (a) and current image (b) of a silicide grain.

Some grains had a ring (crater) like shape (figure3 a). In the centers of such islands fall of conductivitiy was observed (figure 3b). The I-V curves measured in the silicide grains (figure 4) were typical for MOS structures with tunneling transparent insulator [6].

For the sample region annealed at lower T (800<T<900 ºC) where no degradation occurred, no tunneling current through the oxides (both HfO_2 and ZrO_2) was observed up to the gap voltage U=±10 V.

In Figure 4 the morphology and the current images of ZrO_2 film (24 nm) annealed in vacuum to partial degradation are shown.

It should be noted that no correlation between morphology and the current image was observed.

The contrast in the current image points to the layer-by-layer formation of $ZrSi_x$, probably starting from ZrO_2/Si interface. In the Z channel we observed the morphology of ZrO_2 film surface (Figure 5 a,c), which is rather flat over the scanned area. In the current image, the contrast is attributed to the island growth of $ZrSi_x$ at ZrO_2/Si interface (Figure 4, b,d).

It is known, that these oxides have high equilibrium concentration of oxygen vacancies, which increases with increasing T. When annealing in vacuum, vacant oxygen can reach the surface and leave the oxide.

On the other hand, the vacancies can condense with formation of the open-ended nanopores at high concentration. Through these nanopores, oxygen leaves $HfO_2(ZrO_2)$/Si interface into vacuum, as, for example, SiO.

Finally, the restored metal (Hf,Zr) stays on interface in contact with Si. Later upon annealing at elevated temperatures growth of silicide started.

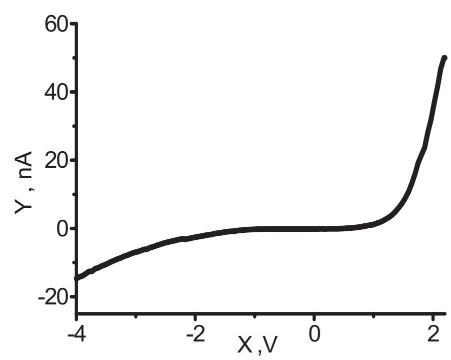

Figure 4: A typical I-V curve of a silicide grain.

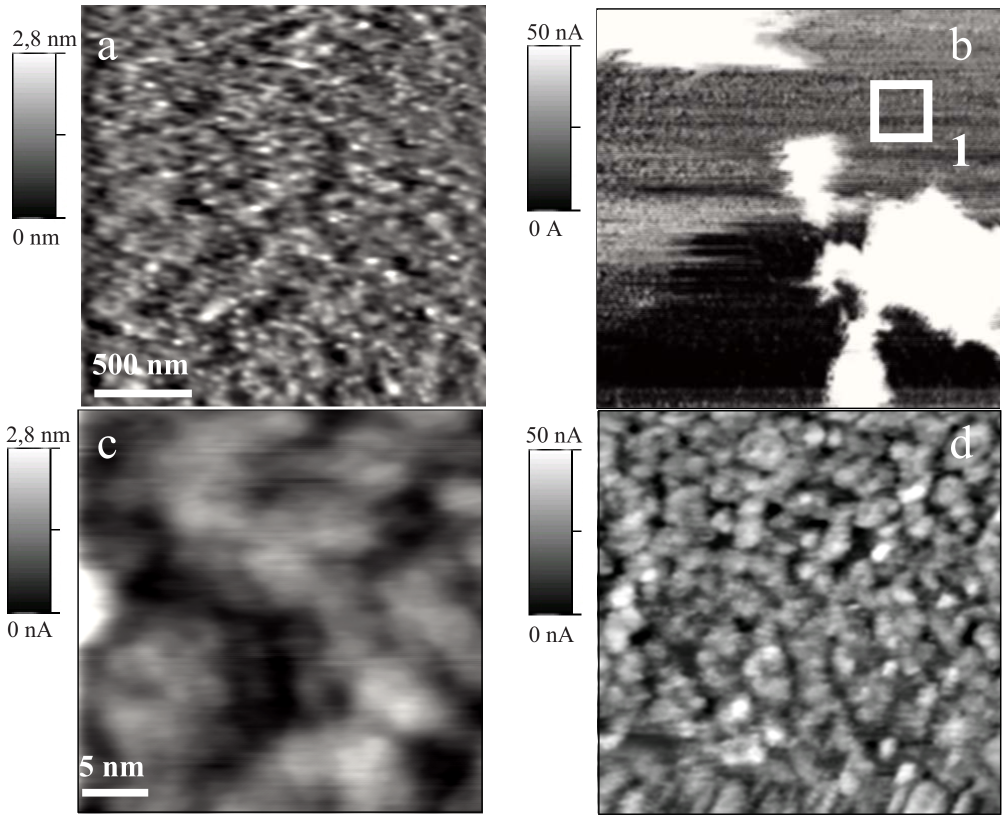

Figure 5: Morphology (a,c) and current image (b,d) of ZrO_2 film (24 nm) after vacuum annealing at T ≈900 °C (c,d are zoom of region 1).

In future, it is possible that investigations of the dependence of the morphology and conductivity of the thin high-k insulator films on the annealing temperature would reveal more important details of the degradation kinetic of such layers in contact with Si.

5 ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support by joint Russian-American BRHE Program sponsored by Russian Ministry of Education and and Science and by US Civilian Research and Development Foundation (CRDF) in parity, Award No. REC-NN-001.

The authors would like to thank Giovanna Scarel from MDM-INFM Laboratory for providing ZrO_2/Si sample used in this work.

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