A neutron reflectivity study of silicon oxide thin films

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The structure and properties of ultra-thin silicon oxides are under constant investigation due to the continuing decrease of the dimensions of elemental components, now reaching 0.1 µm.

This paper focuses on the use of neutron reflectivity, infrared spectroscopy and electrochemistry [1] to characterize silicon oxide thin films.

The films were produced thermally in O_2 atmosphere at high temperature and with a chemical method consisting of immersion in oxidizing baths of basic SC1 solutions (NH_4OH: H2O2: H_2O) or acidic SC2 solutions (HCl: H_2O_2: H_2O) after hydrophobic treatment in HF/HCl. These mixtures are commonly used during the first cleaning steps of the wafers to get rid of inorganic particles and most of the metallic particles. Another method used was to build a thin silicon oxide layer by anodic oxidation in HCl electrolyte. Various applied currents were chosen: 1µA, 3µA and 0.3µA, with different immersion times. All the experiments were undertaken in the dark.

The three types of silicon oxide layers were studied by neutron reflectivity. This technique is able to probe the silicon oxide thickness, density and Si/SiO_2 interface roughness. Silicon and silicon oxide have a good contrast for neutrons, enabling a precise determination of the thickness, roughness and mean density of the oxide layer. Experiments were performed on the white-beam time-of-flight neutron reflectometer Eros [2] at the Leon Brillouin Laboratory at Saclay. The parameters of the layers were obtained by least-mean-squares fitting of the experimental curves. A typical set of data is represented in Figure 1. The surface roughness was less than 0.3 nm for all samples.

From the neutron reflectivity measurements (Table 1), the thickness of the oxides was obtained and, in the case of anodic oxides, compared to that calculated from the Faraday law, knowing the electrical charge passed through the silicon sample. In each case the thickness was found to be almost twice that extracted from the neutron experiments. This result may be related to oxide solubility in both the acidic and basic media.

It appears that the anodic oxides have comparable densities to the thermal oxides. The chemical oxides are less dense, especially the SC2 oxide grown in acidic media. This feature was checked with infrared spectroscopy. Si-O-Si bond vibrations were observed and even those of $Si-H_x$ bonds persisted after a 3-h treatment in SC2 solution, leading to the conclusion that, in this case, oxidation takes place through generation of islands.

Treatment	Thickness (nm)	Si/SiO_2 roughness	Density
Thermal oxide 4.5 nm	4.7 ± 0.3		95 ± 4%
Thermal oxide 2.5 nm	2.9 ± 0.4		77 ± 5%
Thermal oxide 2.2 nm	2.6 ± 0.4		95 ± 5%
Anodic oxide 1 µA for 69420 s	5.8 ± 0.3	1.4 ± 0.4	96 ± 4%
Anodic oxide 3 µA for 70200 s	12.4 ± 0.3	0.9 ± 0.4	76 ± 6%
Anodic oxide 0.3 µA for 69180s	3.8 ± 0.3	2.3 ± 0.4	79 ± 6%
Anodic oxide 0.3 µA for $2.16.10^5$s	4.6 ± 0.3	1.3 ± 0.5	94 ± 6%
SC1 oxide	1.2 ± 0.3		69 ± 6%
SC2 oxide	1.1± 0.3		60 ± 6

Table 1: Thickness, roughness and density of the SiO_2 layer of the samples, obtained by neutron reflectivity.

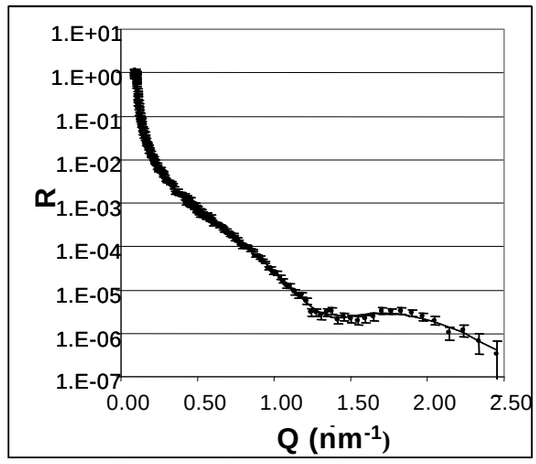

Figure 1: Neutron reflectivity of the thermal oxide sample of 4.5 nm thickness. The continuous line corresponds to the reflectivity calculated from the variation in scattering length density (*Nb*) as a function of the distance *z* from the surface.

References

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