X-ray reflection and emission spectroscopic analysis of Al_2O_3/Si and HfO_2/SiO_2/Si structure

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Introduction

Metal oxides of high dielectric constant are candidates to substitute SiO_2 as a gate dielectric in complementary metal-oxide-semiconductor (MOS) devices. Atomic layer deposition (ALD) is one of the most promising method of forming MOS structures for the development of modern micro and nanoelectronics devices. Because of the extremely small size of the nanostructures, their formation requires the control of the growth process at the monolayer level. Obviously, the electro physical properties of such structures are determined not only by the characteristics of thin film but also by the characteristics of the interface between the insulator film and the semiconductor substrate. In this work we demonstrate the importance of soft X-ray reflection spectroscopy and X-ray emission spectroscopy as nondestructive depth–resolved characterization tools of the local atomic structure of high-k dielectric planar systems.

Methods and Materials

The Al_2O_3 (30 nm) and HfO_2 (5 nm) films were grown on the Si and SiO_2 (0.3 nm)/Si surfaces, respectively, by atomic layer deposition (ALD) method. In both cases the silicon substrates were preliminarily treated in a solution of 1% HF in deionized water. To grow the Al film the reactor was filled by vapors of trimethyl aluminum for a few tenths of a second, with subsequent evacuation of the reagent and admission of water vapor to the reactor, which prepared the surface for the next ALD cycle. To prepare the HfO_2/SiO_2/Si system the silicon surface was slowly reoxidized in a controllable way, using a solution containing HCl and H_2O_2, results in a chemical SiO_2 layer 0.3 nm thick. Then the HfO_2 layer was deposited by ALD using $HfCl_4$ and H_2O as precursors. Transmission electron microscopy (TEM) analysis showed that the HfO_2 and Al_2O_3 layers were amorphous.

X-ray reflection and emission spectroscopy were implemented to characterize both systems. The angular spectral dependences of the reflection coefficient (in both systems) in the vicinity of the O *K*-absorption edge were obtained using an s-polarized synchrotron radiation. The energy resolution was better than 0.1 eV. The dependence of the shape of the Al and Si $L_{2,3}$ emission bands (in Al_2O_3 film) on the primary electron energy were studied using RSL-1500 x-ray spectrometer [1]. The spectra in the range 50-110 eV were obtained with a wavelength resolution of 0.2 nm. The Si $K\beta$ emission was studied in the HfO_2/SiO_2/Si system using the ultra-high vacuum IRIS apparatus [2]. The Si spectrum was analyzed with 4 keV electrons.

Results and Discussion

A. Al_2O_3/Si system

X-ray reflection spectra were measured at different glancing incidence angles in the vicinity of the O K-absorption edge to obtain the information about local physico-chemical environment of the oxygen atoms. The variation of the glancing incidence angle enables the depth profilometry of the sample because the different thicknesses of the layer contribute to the reflected beam at each angle. The data were analyzed using Kramers-Kronig transformation. According to obtained data the Al_2O_3 film is amorphous and is non-homogeneous in the depth.

The phase chemical composition of the Al_2O_3/Si system was studied by depth-resolved X-ray emission spectroscopy. It was established that the investigated film is a layer of mixed Al_2O_3 and SiO_2 oxides, in which silicon dioxide presents even on the sample surface and its concentration increases as one approaches the interface with the substrate. By this means Al_2O_3 film prepared by ALD on an oxide–free surface of a silicon substrate produces an interface containing, nevertheless, a large amount of SiO_2.

B. HfO_2/SiO_2/Si system

X-ray reflection spectroscopic investigation of the HfO_2/SiO_2/Si system performed at different glancing angles in the vicinity of O-K absorption shows that HfO_2 film is characterized by a well defined structure with a thin superficial layer presenting defect points or various local atomic structures.

The physico-chemical state of silicon atoms present in the HfO_2/SiO_2/Si system was studied by X-ray emission spectroscopy induced by electrons [3]. From the analysis of the Si 3p occupied valence states, the very thin oxide interfacial layer is characterized. The silicon oxide thickness is determined to be one or two monolayers.

[1] A.P. Lukirskiy, V.A. Fomichev, and A.V. Rudnev, Appar. Metody Rentgen. Anal. **9**, 89 (1970).

[2] C. Bonnelle, F. Vergand, P. Jonnard, J.-M. André, P. Avila, P. Chargelègue, M.-F. Fontaine, D. Laporte, P. Paquier, A. Ringuenet, B. Rodriguez, Rev. Sci. Instrum. **65**, 3466 (1994).

[3] P. Jonnard, I. Jarrige, O. Renault, J.-F. Damlencourt, F. Martin, Surf. Sci. **572**, 396-400 (2004).