



Evolution of Zr/Hf/Zr trilayers during annealing studied by RBS

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ABSTRACT

The Zr/Hf system is highly interesting due its various applications, e.g. formation of amorphous ternary alloys, superconductive properties and production of gate oxide layers with high dielectric coefficients by oxidation of Zr/Hf multilayers. In this work Zr/Hf/Zr trilayers with an individual layer thickness of approximately 50 nm were deposited by electron gun evaporation on a substrate consisting of silicon covered by a micrometer thick thermal oxide layer. Samples were subjected to annealing procedures at 500 and 1200 °C in flowing air atmosphere to promote oxidation and Zr/Hf interdiffusion effects.

RBS studies of the as-deposited and annealed samples were performed at the van-de-Graaff accelerator of ITN using He⁺ and H⁺ beams with energies between 2.0 and 2.525 MeV in order to study compositional changes induced by the heat treatment. In the case of low-temperature annealing the layer system appears, besides the oxidation process starting from the surface, to be stable. On the other hand, high-temperature annealing leads to an asymmetric Hf-diffusion into the surface and interior Zr-layer provoked by anomalous diffusion due to a phase transition in Zr accompanied by an almost complete oxidation of the layer structure. Oxygen and metal depth distributions obtained by RBS in the as-deposited and treated samples are provided.

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1. Introduction

The zirconium-hafnium system is an interesting case for many studies in basic and applied solid-state physics due to the chemical and structural similarity of the two elements, which results in the possibility of formation of alloys over the full mixing range. Zr–Hf layers were intensively studied in ion beam mixing experiments [1–3] due to their high cohesive energies and the negligible heat of mixing. Also the superconductive properties of Zr–Hf-multilayers have drawn interest in the system [4]. Although Zr and Hf do not form amorphous alloys themselves solid-state reactions with other metals, e.g. Ni, produce ternary amorphous alloys at relatively low temperatures [5]. Recently, the need for new high-*k* dielectric gate materials for the CMOS technology has triggered intense research work on the formation of oxides and silicates based on Zr, Hf [6] and Zr–Hf multilayers [7].

In this work we present studies on the effects of heat treatments at low (500 °C) and high (1200 °C) temperature in air on a Zr–Hf–Zr trilayer system with regard to oxidation and metal diffusion which are expected to compete with each other.

2. Experimental details

The Zr/Hf/Zr trilayer system was deposited under ultrahigh vacuum conditions by electron gun evaporation from metallic targets on an oxidized silicon substrate. The silicon oxide layer was produced by thermal oxidation and has an expected thickness of approximately 1 μm. The deposition parameters for the metal layers were chosen to achieve an individual layer thickness of about 50 nm.

The multilayer structures were subjected to heat treatments in flowing air atmosphere in a conventional furnace. The treatments were performed at 500 °C (low-temperature regime in which Zr and Hf are in the hexagonal crystal phase and where oxidation is expected to be the dominating process) and 1200 °C (high-temperature regime at which Zr has undergone a phase transition into the cubic crystal structure and where oxidation and metal diffusion are expected to compete strongly).

For the determination of the thickness and investigation of the compositional changes as a function of depth Rutherford backscattering spectrometry (RBS) measurements were done at the van-de-Graaff accelerator at Sacavém. The ion beam impinged at normal incidence on the targets (in order to be able to study the whole layer structure) and the backscattered ions were detected by a detector located at 140° with respect to the incoming beam in IBM geometry. For the measurements He⁺ ion beams with energies of 2.0, 2.3 and 2.525 MeV and H⁺ beams with 2.0 MeV were used.

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The 2.525 MeV He^+ beam allowed the use of the small resonance in the scattering at ^{16}O occurring at 2.484 MeV [8] which facilitated the detection of oxygen in the surface region of the samples. An additional measurement with a proton beam allowed the accurate determination of the SiO_2 buffer layer thickness.

The experimental data were fit using the RUMP program [9]. Since no experimental values for the non-Rutherford scattering of protons and helium ions at oxygen are available for the scattering angle of 140° it was necessary to use calculated cross section values that were obtained by using the SigmaCalc program [10] and to convert them to the proper format for usage with RUMP.

3. Results and discussion

Fig. 1 shows the RBS spectrum of the as-deposited sample recorded using a 2.525 MeV He^+ beam. Using this beam energy the three metallic layers (surface Zr, Hf and interior Zr) appear well-separated from each other and the part of the spectrum belonging to the silicon oxide buffer layer and the silicon substrate.

In the amplified part of the spectrum (showing the RBS-signal of Si and O) one notices a contribution that corresponds to Si and O at the surface. A more detailed analysis shows that this part of the spectrum is due the occurrence of SiO_2 in a part (ca. 5%) of the surface area. The existence of pinholes from the growth process is unlikely due to the total thickness of the metallic multilayer (150 nm). Also an intermixing between the metallic layer and the silicon oxide during the deposition process can be excluded. Therefore this SiO_2 contribution may be attributed to exfoliation due to insufficient adherence of the multilayer. For the further analysis a SiO_2/Si layer spectrum that corresponds to this contribution was calculated separately and then added to the fit for the actual layer structure.

The fit procedure for the part of the spectrum attributed to the metallic trilayer revealed that the surface Zr-layer had undergone notable oxidation during storage at room temperature in air ambient. Further it was found that the Zr-layers contain ca. 2.5% Hf which is a typical value for this material due to the extremely high chemical similarity of the two elements. Although more correctly assigned as Zr(Hf) the layers will be simply referred to as Zr-layer in the remainder of the paper. It is likely that the Hf-layer in the as-deposited sample contains a small amount of Zr but due to the much higher mass of the Hf this could not be verified. Also the influence of a small Zr impurity in Hf on the RBS spectra is expected to be negligible. At the time of measurement the surface

Zr-layer actually consisted of a 17 nm ZrO_2 layer on top of a 44 nm Zr metallic layer. From this the thickness of the original (non-oxidized) surface Zr-layer has been calculated to have been 55 nm. The Hf-layer and the interior Zr-layer show no oxidation and their thicknesses have been determined to be 52 and 64 nm, respectively. The results were cross-checked with measurements at 2.3 MeV He^+ (not shown) for consistency.

To obtain a higher accuracy in the determination of the SiO_2 buffer layer an additional RBS-measurement with a 2.0 MeV proton beam was performed (see Fig. 2) resulting in a thickness value of 975 nm. All layer thickness values agree well with the ones expected from the parameters for the thermal oxidation and deposition processes.

The RBS spectrum obtained for the sample after heat treatment at 500°C (in the same experimental conditions as above) is depicted in Fig. 3. In contrast to Fig. 1 the RBS-signals related to the surface Zr-layer and the Hf-layer are no more separated. This and the clear change in the oxygen signal indicate the progress of the oxidation through the metallic trilayer system.

The RUMP analysis (using the same procedure for the SiO_2/Si contribution at the surface) showed that the surface Zr-layer is already fully oxidized and substantial oxidation of the Hf-layer occurred while the interior Zr-layer seems to be still fully metallic. While in the as-deposited case the oxygen profile in the surface Zr-layer can be described as box-like with a sharp interface, in the case of the Hf a fit to the experimental spectrum can only be obtained by assuming an error-function shaped oxygen distribution as expected for a slow diffusion process as expected due to the moderate diffusion coefficient ($4 - 9 \times 10^{-21} \text{ m}^2 \text{ s}^{-1}$) at this temperature [11]. An average composition for the layer of $\text{HfO}_{1.81}$ was obtained. A detailed oxygen profile (as used in the RUMP fit) for this sample is depicted in Fig. 4. Although the nominal composition at the interface to the interior Zr-film is $\text{HfO}_{1.64}$ there is no indication that oxygen has entered into this film and, instead, a sharp interface occurs. The Hf-film seems to inhibit the further diffusion of the oxygen due to its larger affinity to oxygen.

Further, there is no indication that any interdiffusion of hafnium and zirconium at this interface occurs. This is to be expected since the diffusion coefficient for Hf in the hexagonal α -phase of Zr at a temperature of 500°C is supposed to be extremely small (in the order of $10^{-24} \text{ m}^2 \text{ s}^{-1}$ [12]).

The thickness of the fully oxidized surface Zr(Hf)-layer has been determined to be 85 nm (assuming area densities, for 1 nm, of $8.32 \times 10^{15} \text{ at. cm}^{-2}$ and $8.31 \times 10^{15} \text{ at. cm}^{-2}$ for stoichiometric zirconium and hafnium dioxide, respectively). Since no density

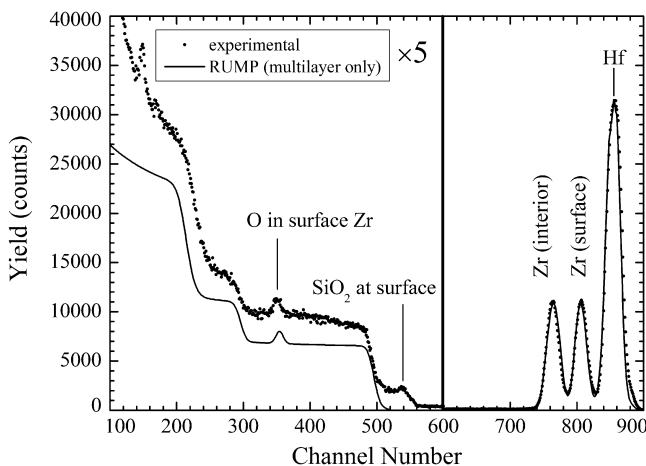


Fig. 1. RBS spectrum of the as-deposited sample taken using a 2.525 MeV He^+ beam in normal incidence and the corresponding RUMP fit (without surface SiO_2). The low-energy part of the spectrum is amplified by a factor of 5.

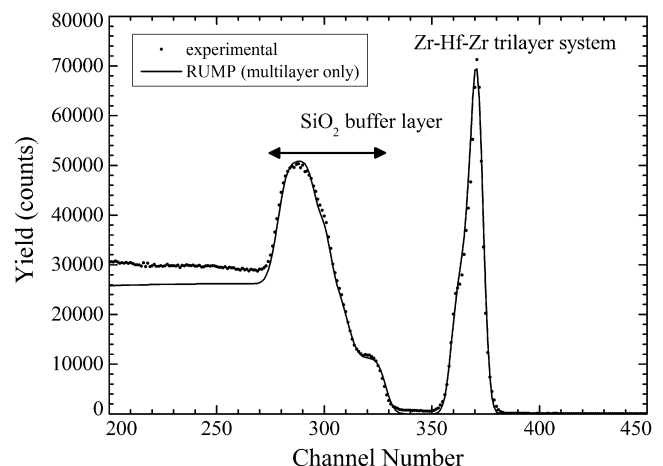


Fig. 2. RBS spectrum of the as-deposited sample taken using a 2.0 MeV H^+ beam in normal incidence and the corresponding RUMP fit (without surface SiO_2).

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