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High resolution Rutherford Backscattering Spectrometry investigations of ZrO_2 layer growth in the initial stage on native silicon oxide and titanium nitride

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ABSTRACT

High Resolution Rutherford Backscattering Spectrometry (HR-RBS) with a depth resolution of about 0.3 nm near the surface was used to analyse the interface between ultrathin high-*k* ZrO_2-layers and the substrate. In order to improve the quality of the analysis, a method was developed that takes local thickness variations, obtained by atomic force microscopy, into account during simulation of the HR-RBS spectra. The initial stages of atomic layer deposition (ALD) growth processes on Si(100) covered with native silicon oxide (SiO_2) or with TiN have been studied. In the first case the interface is sharp, except for a small intermediate $ZrSiO_4$-layer, and no diffusion of Zr-atoms in SiO_2 could be detected. A quite different behaviour could be derived from high resolution spectra for the growth of ZrO_2 on TiN. In addition, measurements of the surface topography of the TiN-layer revealed non-negligible surface roughness. Diffusion of Zr into polycrystalline TiN was demonstrated after correction for surface roughness. This observation indicates that already during the first ALD reaction cycle a small proportion of the deposited Zr-atoms diffuses – probably along grain boundaries – into the TiN-layer up to a depth of 3 nm.

1. Introduction

The interest in the development of nanoelectronic memory devices with an increasing degree of integration leads to a continuous miniaturisation of lateral feature sizes. The reduction of the lateral size results in an undesirable decrease of the capacity of dynamic random-access memory cells that can be compensated by a reduction in the dielectric layer thickness. The shrinkage to less than 1.6 nm using SiO_2 in conventional capacitors results in a steep increase of the direct tunnelling current [1]. Another possibility to increase the capacity is the use of high-*k* materials. Besides HfO_2 the high-*k* dielectric ZrO_2 is a good candidate for the replacement of SiO_2 to be used in the so-called Metal-Insulator-Metal (MIM) capacitors because of the high *k* value and good thermal stability [2–4]. An established method for the conformal deposition of thin high-*k* layers is atomic layer deposition (ALD) [4,5]. The electrical performance of memory cells containing such high-*k* layers depends on a variety of factors like insulator thickness and quality of the interfaces to the metal electrodes. Adverse inhomogeneous electric field distributions within the capacitors are formed by local thickness variations and elemental diffusion at the interfaces with the top and bottom electrodes of the MIM structures, which are often made from TiN [6,7].

Information about the composition, layer thickness and quality of the interfaces is needed for the development of MIM devices. However, not many techniques can provide this information for very thin layers, as it requires a depth resolution of less than 1 nm. One technique that can yield this information is High Resolution Rutherford Backscattering Spectrometry (HR-RBS) [8–11]. This is based on RBS, a well-known, quantitative and standard-free ion beam analysis method, with an improved energy resolution to obtain a high depth resolution. There are many factors influencing the depth resolution in RBS [12]. The two most important factors are the detector resolution and energy straggling. Energy straggling is a physical process arising from the statistical nature of the slowing down of ions in matter. Energy straggling increases with the length that an ion travels through matter and, thus, causes the energy resolution to deteriorate as a function of depth. It is inherent to the analytical process and is therefore unavoidable. The other main factor is the detector resolution and this can be improved by using an appropriate detection system. At the Helmholtz-Zentrum Dresden-Rossendorf, a Browne-Buechner type magnetic spectrometer is used for high depth resolution measurements [13,14]. In the case of ZrO_2, a depth resolution of about 0.3 nm at the sample surface is realised by this detector. This is well-suited for the analysis of ultrathin layers and for depth profiling of embedded heavy elements at interfaces close to the surface. However, effects like thickness variations and substrate surface roughness complicate the correct interpretation of high resolution spectra. These cause features in the spectra that are hardly distinguishable from diffusion profiles. Therefore, a general procedure has been developed that takes local thickness variations

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and surface roughness of the layers into account in the simulation of HR-RBS spectra.

Here, the application of the HR-RBS simulation method described above to the analysis of the early stages of growth of ZrO_2 layers by ALD on SiO_2/Si and on TiN/Si substrates is reported. Native silicon oxide on silicon (hereafter called SiO_2 or native SiO_2) is chosen as a simple well-known system, whereas the TiN substrate is of most scientific interest. It is assumed that native silicon oxide has a composition of SiO_2 at the surface, however changes in composition do not influence the results obtained in this work.

2. Experimental details

Ultra-thin zirconium dioxide films of different thicknesses were prepared by ALD on Si substrates covered either with native SiO_2 or a CVD (chemical vapour deposition) grown TiN film of 20 nm nominal thickness. TEMAZ (Tetrakis-ethylmethylamino-zirconium, $Zr[N(CH_3)(C_2H_2)]_4$) and ozone (O_3) served as precursor and second reactant, respectively, for the ALD growth process of ZrO_2 at a substrate temperature of 275 °C [7,14]. The deposition temperature is much lower than that used by ALD for other high-*k* materials like Al_2O_3 [6]. The TiN film was grown by standard CVD at 400 °C.

The interface studies and the determination of the areal density of Zr were carried out by HR-RBS in forward direction. A 2.02 MeV C^{2+}-ion beam from a 3 MV Tandetron™ accelerator was used for the analysis. Carbon ions were chosen over commonly used He ions because of the higher stopping power and higher scattering probability. The first increases the depth resolution, whereas the latter reduces the fluence for a given statistical uncertainty. Possible sample damage during the measurement increases for higher mass ions but carbon is still a sufficiently light atom that this effect does not undo the advantages of using carbon ions.

The angle of incidence of the ion beam is 17.5° with respect to the sample surface. The scattered ions were detected at a scattering angle of 35.8° using a magnetic spectrometer of Browne-Buechner type (Fig. 1) [14]. In such a detector the scattered ions traverse a dipole magnet on a circular path due to the Lorentz force. On leaving the magnet, the ions are separated according to their energy. The energy after scattering can then be determined from the position of the ions after exiting the magnet. In this way an energy resolution of about 4 keV is achieved, which results in a depth resolution of about 0.3 nm at the surface. For the angle of incidence, a small value is chosen to maximise the path lengths of the ions and, therefore, the depth resolution, but not so small that the influence of the surface roughness becomes unacceptably large because the probability that the ions traverse hillocks before scattering on the sample surface increases for smaller incidence angles (see Fig. 2). Forward scattering is applied to maximise the scattering cross-section and, thus, the sensitivity for a given fluence. For all HR-RBS measurements, the area of analysis was about 1 cm^2 so that the C^{2+}-ion fluence could be kept sufficiently low ($<2.3\times10^{14}$ ions/cm^2) in order to avoid interface mixing [15]. In addition, the surface topography of the ultra-thin zirconium oxide films was examined by Atomic Force Microscope (AFM), using a Veeco Instruments device equipped with a silicon tip (10 nm radius of curvature) in tapping mode. Areas of 0.5×0.5 μm^2 were scanned at a rate of 1 Hz and a resolution of 10 bit.

3. Analysis with roughness correction

In the HR-RBS experiment based on a magnetic spectrometer, ions with different energies are separated spatially after traversing the magnet and detected with a position-sensitive detector. The resulting spatial scale of the spectrum is then converted into an energy scale [15]. Afterwards, the analysis of the RBS spectra is performed with the widely used program SIMNRA [16]. In this program a model of the sample is used to obtain a simulated spectrum. This spectrum is compared to the measured spectrum and the sample model is adapted until a good agreement is reached. It should be noted that the layer thickness directly obtained from the analysis is an areal density in atoms/cm^2. This has to be converted to the layer thickness in nm with a given or estimated density and composition. Therefore the uncertainty in the density directly translates into the uncertainty in thickness in nm but this does not influence the quality of the simulation.

An important effect influencing the analysis result of HR-RBS is surface roughness, in particular due to layer thickness fluctuation. In order to separate the roughness from effects caused by features of the sample like diffusion or interface mixing, it has to be determined, e.g. by AFM. The roughness data can be used for corrections in the analysis. The roughness correction in SIMNRA, however, neglects correlation effects induced by glancing incident ions passing through a hillock before scattering on the surface. Traversing a hillock can also take place after scattering or even take place multiple times. Thus, SIMNRA simulations with roughness corrections are only correct for

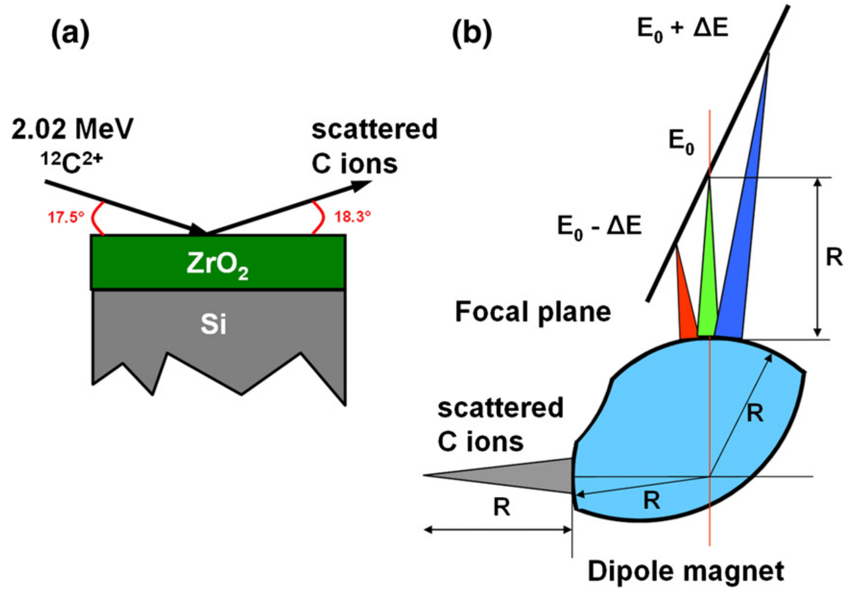

Fig. 1. Schematic of the measurement layout (a) and of the detector configuration (b).