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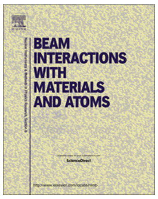

Oxygen depth profiling with subnanometre depth resolution

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ABSTRACT

A High-depth Resolution Elastic Recoil Detection (HR-ERD) set-up using a magnetic spectrometer has been taken into operation at the Helmholtz-Zentrum Dresden-Rossendorf for the first time. This instrument allows the investigation of light elements in ultra-thin layers and their interfaces with a depth resolution of less than 1 nm near the surface. As the depth resolution is highly influenced by the experimental measurement parameters, sophisticated optimisation procedures have been implemented. Effects of surface roughness and sample damage caused by high fluences need to be quantified for each kind of material. Also corrections are essential for non-equilibrium charge state distributions that exist very close to the surface. Using the example of a high-k multilayer $SiO_2/Si_3N_4O_x/SiO_2/Si$ it is demonstrated that oxygen in ultra-thin films of a few nanometres thickness can be investigated by HR-ERD.

1. Introduction

In many cases in material science, such as the development of new coatings or new material properties through surface modification, it is important to know the changes of the chemical composition as a function of depth. The depth information has to be known with nanometre resolution, especially at the interfaces, for such applications as high-k layers for the semi-conductor industry [1], multilayer stacks for X-ray mirrors [2], etcetera (e.g. [3]). There is an increasing demand for the determination of the (high-depth resolution) concentration profiles for light elements like B and O [4,5].

Ion beam analysis (IBA) is a very suitable analytical technique to determine concentration depth profiles [6]. The depth information is obtained by the specific energy loss of swift ions passing through the material to be analysed. Ion scattering methods can be employed for determination of the chemical composition of thin films with an uncertainty at the percent level, especially at ion energies in the MeV range [6]. Therefore, Rutherford Backscattering Spectrometry (RBS) has been established as a standard analytical method for measuring the depth concentration profiles of heavy elements in lighter thin films.

Depth profiles of light elements in heavier thin films can e.g. be determined by Elastic Recoil Detection (ERD) [7], an IBA method that commonly uses heavy ions. Main advantages of IBA methods are that they are quantitative, standard-free and essentially non-destructive in the sense that the measurement results are not distorted and no material is consumed if the measurement conditions are chosen carefully [6]. Although one has to be aware of possible artefacts caused by the analysing beam. Alterations might occur in the chemical composition in case of volatile components, in the interface quality (mixing), or even in the crystallinity of certain materials (partial amorphisation). In contrast to more widespread depth-sensitive analytical methods such as secondary ion mass spectrometry (SIMS), ERD does not need any reference material for calibration. Based on the well-known elastic scattering cross-section [8], the concentration versus depth of any element can be deduced from the measured energy spectrum of the recoiled ions. The cross-section is based on the screened elastic coulomb repulsion of two nuclei and can be calculated analytically. Thus, ERD is often used as a primary method to provide calibration for other analytical methods [9]. A disadvantage of ERD is that it does not give any information about the chemical bonds in the sample or the oxidation state of the individual elements. However, this can also be regarded as advantageous, since the total concentration of an element is obtained independently of chemical bonds [6,10].

The depth resolution of conventional ERD is limited by several parameters [11]. It correlates directly with the energy resolution of the detector, because the depth scale is defined by the energy loss of energetic heavy ions interacting with matter. The detector energy resolution is limited by statistical processes during generation of electron–hole-pairs in silicon detectors or free electrons in ionisation chambers, and by electronic noise. Hence, the energy

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resolution of the conventional detectors is typically in the range of $\Delta E/E = 1\%$ [12,13]. High-energy resolution leading to high-depth resolution is either obtained using Time-of-Flight systems (TOF) [14,15], or electrostatic and magnetic spectrometers [16], where the energy information is transformed into position information.

Since 1990 several spectrometers for high-resolution RBS/ERD have been built and successfully employed, e.g. an electrostatic cylindrical analyser [17] and several magnetic spectrometers [18–25]. A Browne–Buechner type magnetic spectrometer is used at the Helmholtz-Zentrum Dresden-Rossendorf (HZDR) 3 MV tandem accelerator for high-resolution RBS [21,26].

However, this Browne–Buechner type spectrometer is not useful for ERD analyses, since the necessary large solid angle together with a kinematic correction cannot be implemented. For ERD with high-depth resolution a new magnetic spectrometer ("QQDS") was developed and employed for the analysis of light elements. Various parameters and effects influencing the depth resolution are discussed in detail. The first element investigated with the "QQDS" is oxygen and results of quantitative depth profiling in a $SiO_2/Si_3N_4O_x/SiO_2/Si$ multilayer are presented and compared to conventional ERD measurements.

2. Experimental details

2.1. Experimental set-up

The essential part of the high-depth resolution ERD set-up at HZDR is a QQDS magnetic spectrometer transferred from the former Forschungszentrum Karlsruhe [27]. It consists of a magnetic dipole to disperse particles according to their momentum, two quadrupole magnets to form an image in the dispersive and non-dispersive plane, and one sextupole magnet to rotate the focal plane parallel to the exit of the dipole. The arrangement is two quadrupoles first, followed by the dipole and finally the sextupole (Fig. 1), hence the abbreviation QQDS. The rotatable mounting of the spectrometer allows adjusting different scattering angles $\Theta_{\text{HR-ERD}}$.

As for conventional ERD, ion beams, typically Cl or Cu ions are generated by a 5 MV-tandem accelerator. The beam energy is stabilised by a feedback system with current measurements on slits behind a 90° analysing magnet. The beam fluence is obtained from a rotating vane in front of the target chamber. The vane is coated with a thin gold layer and intercepts part of the beam. Ions backscattered from the rotating vane are measured by a silicon detector that is calibrated against a Faraday Cup at the beginning of each measurement series.

The target chamber contains a Faraday Cup for calibration of the rotating vane arrangement, a 5 axis-goniometer, two 4-slit assemblies for beam alignment, a load-lock, a cold trap, a residual gas analyser (QME220), and a large 880 L/s turbo molecular pump. The chamber has five flanges for discrete mounting positions of the spectrometer ($\Theta_{\text{HR-ERD}} = 0°, 15°, 30°, 45°, 60°$). In addition, there are a separate ΔE-E ERD Detector ($\Theta_{\text{ERD}} = -30°$) and a compact ΔE-E-detector ($\Theta_{\text{ERDcoinc}} = 30°$) that can be used simultaneously with the spectrometer to obtain a low-resolution overview measurement. The cold trap is filled with liquid nitrogen and primarily used to reduce the partial vapour pressure of water in the target chamber. This and other residual gases are continuously monitored by a residual gas analyser.

The High-depth Resolution ERD (HR-ERD) detector consists of a position sensitive proportional counter [28] to determine the position of the ions after exiting the magnets and a Bragg Ionisation Chamber (BIC) to distinguish different elements. Isobutane (2-methylpropane, quality 3.5) is used as ionisation gas at the same pressure for both parts. The detector is operated in flow-mode so that the gas is constantly replaced. The entrance window of the detector is a 70 μg/cm^2 stretched polypropylene membrane supported by a steel grid. The position sensitive readout of the proportional counter is realized by a high resistance anode wire made of $NiCr_{20}AlSi$ alloy (Isabellenhütte Heusler GmbH). The readout is realised on both ends of the wire providing the position from the charge division. The effective length that can be used for the analysis is 80 mm. With a dispersion of 23.8 mm/%, this leads to an energy range $\Delta E/E$ of 6.7% for one measurement. The maximum solid angle, which is limited by the bore diameter of the quadrupole lenses, is $\Omega_{\text{HR-ERD}} = 1.1$ mSr. There are two preamplifiers (Canberra2006) for the position signals and one preamplifier (Canberra2006) for the BIC. The main amplifier of all detectors is a 16-channel-shape-amplifier (Caen N5688). Finally, for digitalisation of the signals, an MPA-3 system (analog-to-digital-converter, software and interface module, FAST ComTec) is used. Since the evaluation of four signals from two detectors is quite complex, post data-acquisition processing is essential.

The goniometer has two rotational and three translational axes. To limit sample damage, the sample can be moved during the measurements, thus, enlarging the investigated area.

The calculation of the individual magnetic fields is performed by the so-called transfer matrix method [29]:

$$\vec{x}_0 = M_{G5} \cdot M_S \cdot M_{G4} \cdot M_D \cdot M_{G3} \cdot M_{Q2} \cdot M_{G2} \cdot M_{Q1} \cdot M_{G1} \cdot \vec{x}_i \tag{1}$$

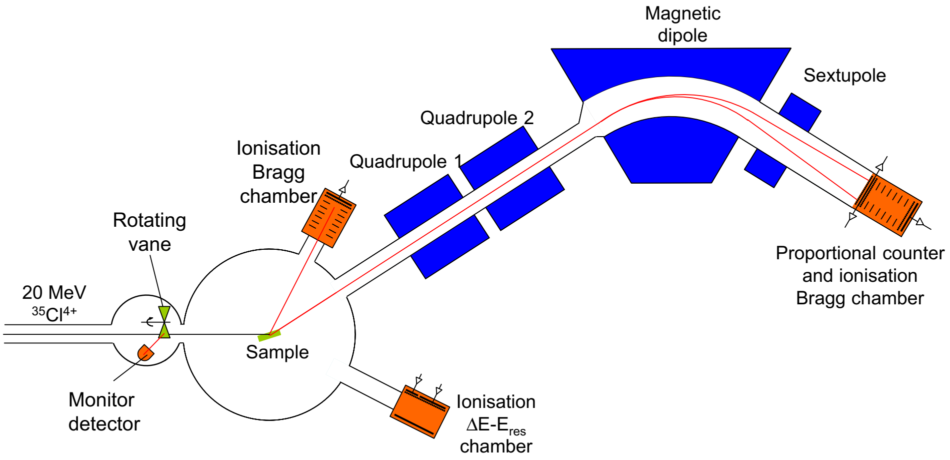

Fig. 1. Schematic diagram of the high-resolution ERD set-up QQDS at HZDR.