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Determination of molecular stopping cross section of ^{12}C, ^{16}O, ^{28}Si, ^{35}Cl, ^{58}Ni, ^{79}Br, and ^{127}I in silicon nitride

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ABSTRACT

Silicon nitride is a technologically important material in a range of applications due to a combination of important properties. Ion beam analysis techniques, and in particular, heavy ion elastic recoil detection analysis can be used to determine the stoichiometry of silicon nitride films, which often deviates from the ideal Si_3N_4, as well as the content of impurities such as hydrogen, even in the presence of other materials or in a matrix containing heavier elements. Accurate quantification of IBA results depends on the basic data used in the data analysis. Quantitative depth profiling relies on the knowledge of the stopping power cross sections of the materials studied for the ions involved, which in the case of HI-ERDA is both the primary beam, and the recoiled species. We measured the stopping cross section of ^{12}C, ^{16}O, ^{28}Si, ^{35}Cl, ^{58}Ni, ^{79}Br, and ^{127}I in a well-characterised silicon nitride membrane. The measurements were made by independent groups utilising different experimental setups and methods. In some cases there is extensive overlap of the energy range in different experiments, allowing a comparison of the different results. The four independent data sets reported in this work are in excellent agreement with each other, in the cases where similar energy ranges were measured. On the other hand, the data are in most cases higher than calculations made with the interpolative schemes SRIM and MSTAR together with the Bragg rule. Better agreement is found with MSTAR in some of the cases studied. This work is a significant extension of the heavy ion stopping power data base for silicon nitride.

1. Introduction

Silicon nitride is a technologically important material in a range of applications due to a combination of important properties. Very good thermal shock resistance, high fracture toughness, temperature strength, creep resistance and oxidation resistance, together with a low thermal expansion coefficient and low density, make it a widely used material in a variety of products such as high performance bearings, cutting tools, and engine components [1,2]. On the other hand, silicon nitride is also used in the microelectronics industry as a high permittivity dielectric, as a passivation or protective barrier due to its low permeation to alkali and small ions, and as an etch mask in micromachining [3–5].

Ion beam analysis (IBA) techniques play an important role in developing and optimising systems that include silicon nitride [6]. In particular, heavy ion elastic recoil detection analysis (HI-ERDA) can be used to determine the stoichiometry of silicon nitride films, which often deviates from the ideal Si_3N_4, as well as the content of impurities such as hydrogen, even in the presence of other materials or in a matrix containing heavier elements [7,8].

Accurate quantification of IBA results depends on the basic data used in the data analysis. Quantitative depth profiling relies on the knowledge of the stopping power cross sections of the materials studied for the ions involved, which in the case of HI-ERDA is both the primary beam, and the recoiled species. Even if new stopping power measurements are continuously being published [9,10], the stopping powers are almost always taken from the interpolative scheme SRIM [11], which is geared towards individual elements and not molecules. The Bragg rule is usually employed to

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calculate the molecular stopping power based on the elemental values [12]. For heavy ions, the accuracy of this procedure is variable, with experimental values agreeing well with the SRIM prediction in some cases, and less well in other cases. MSTAR is another interpolative scheme [13], based on a different set of experimental data, and also geared mainly towards elemental stopping. MSTAR does not include data for all ions.

We have measured the stopping cross section of ^{12}C, ^{16}O, ^{28}Si, ^{35}Cl, ^{58}Ni, ^{79}Br, and ^{127}I in a well-characterised silicon nitride membrane, in the context of a Coordinated Research Project of the International Atomic Energy Agency, where many other systems were measured [14–16]. The measurements were made by independent groups utilising different experimental setups and methods. In some cases there is extensive overlap of the energy range in different experiments, allowing a comparison of the different results.

2. Methodology

2.1. Experimental details

The stopping cross section measurements employed in all cases the direct transmission technique [17,18]. For particle detection, each participating laboratory used its own detection system. Helsinki employed a ToF telescope, consisting of two carbon-foil timing gates separated by a 684 mm flight length and an Ortec Ultra series ion implanted detector [19]. The sample foils were placed between the second timing gate and the energy detector. Elemental bulk targets of Ge and Re were used to forward scatter the projectile ions. The ions are scattered from a range of depths in the targets, and therefore have a continuous range of energies, from a maximum slightly below the initial beam energy, down to zero [20]. Measurements are made with and without the silicon nitride membrane in position. The energy before the foil is determined with the ToF detector and the energy after the foil by the particle detector, leading to the determination of a continuous stopping power curve.

Jyväskylä used a ToF-E telescope at a 1.7 MV Pelletron, with good detection efficiency for H, higher than 90% for He, and higher than 99.5% for C. The timing resolution was 155 ps measured for He (FWHM). A gas ionisation detector was used for the energy measurement. The data acquisition was realised in list-mode, and a data stamp with an accuracy of 25 ns was given for each event. Coincident events are determined off-line. The primary beam was scattered from a 1 nm Au layer on Si substrate and this scattered beam either went through the silicon nitride membrane or it was scattered directly to the ToF-E telescope.

At iThemba LABS [20], a mass dispersive Time of Flight (ToF) spectrometer was used, consisting of two carbon foil based Microchannel Plate (MCP) timing detectors 0.6 m apart, and a passivated implanted planar silicon (PIPS) semiconductor energy detector at the end of the flight path just behind the second time detector. The ToF telescope sits at 30° to the incident beam direction. The ions whose energy loss is measured could either be incident projectile ions from the accelerator, scattered by a suitable heavy target element, or recoil ions ejected from the target by the incident beam. In either case the beam of ions incident on the stopper foil has a continuous range of energies. Measurements were done with and without the foil, positioned between the ToF and the PIPS detector [20]. In this case, the data was divided in energy bins and the stopping power was calculated for selected points.

Munich used the Q3D magnetic spectrograph at the Munich tandem accelerator [21]. The main features of the Q3D magnetic spectrograph are its large dispersion ($dE/(Edx) \approx 2 \times 10^{-4}$/mm), the high intrinsic resolution ($\Delta E/E = 2 \times 10^{-4}$), the large solid angle of detection (up to 14.3 msr) and, most importantly, the possibility to correct for the kinematical shift up to the fourth order, by means of a magnetic multipole element. Routinely, the kinematic shift is corrected up to the third order, leading to an overall energy resolution of 7×10^{-4} even when a large solid angle of detection of 5 msr is used. Without correction the kinematical shift would be larger than 6% energy spread at the usually used mean scattering angle of 15°. At the end the multipole element is adjusted in such a way that the recoil ions scattered from a certain depth are focused to a certain position of the focal plane of the Q3D where the ions are identified and their position is measured. Thin foil targets were mounted for the stopping measurements perpendicular to the incident beam. After passing the thin foils, the energy loss of the ion beam is analysed with the Q3D spectrograph at 0° scattering angle.

All taken together, experiments were made for ^{12}C, ^{16}O, ^{28}Si, ^{35}Cl, ^{58}Ni, ^{79}Br, and ^{127}I. The energy range was different for different ions, but always in the range useful for IBA (see Table 1).

2.2. Silicon nitride membranes

A key issue in the experimental determination of stopping power is the availability of adequate targets. These must be very well characterised. In particular, in transmission or thin film experiments, their thickness and areal density must be well known, as it directly influences the results obtained. Surface roughness, the presence of impurities, and the exact stoichiometry in multielemental targets, are also important parameters.

Commercially available silicon nitride membranes were acquired [22], with thicknesses of 30 and 100 nm. The manufacturer information stated that real thickness values can deviate up to 10%, with a batch-to-batch variation up of 3–4%. However, within a batch, adjacent wafers are very similar in thickness, and the variation across a single wafer is better than 1%; membranes for a single order are supplied from a single batch. Across a single membrane, the thickness variation will be much better than 1%. Finally, the membrane roughness should be low, around 5 Å. These parameters are ideally suited for energy loss measurements and to be used as substrates for deposition of thin films of other materials, provided that the actual areal density of the membranes used is measured.

The composition of the membrane was determined with an HI-ERDA experiment made at the Munich Q3D magnetic spectrograph [21] using a 150 MeV ^{127}I beam, with a ΔE–E detection system at a 38° scattering angle. The results are given in Table 2, where the statistical uncertainties are also given. However, there are other sources of uncertainty, which need to be taken into account, and we elaborated an uncertainty budget, summarised in Table 3.

Table 1
Experiments performed: ions used, energy ranges, and institute.

Ion	Energy range (MeV)	Institute
^{12}C	1.89–5.05	iThemba
^{16}O	2.11–6.90	iThemba
^{28}Si	3.56–8.71	iThemba
^{35}Cl	34.9	Munich
^{58}Ni	59.7	Munich
^{79}Br	39.7	Munich
^{12}C	0.56–9.92	Helsinki
^{16}O	0.33–7.88	Helsinki
^{35}Cl	0.53–19.72	Helsinki
^{79}Br	2.99–42.49	Helsinki
^{127}I	4.12–37.1	Helsinki
^{12}C	0.20–8.16	Jyväskylä
^{16}O	0.26–8.08	Jyväskylä
^{35}Cl	0.59–10.89	Jyväskylä