Thin Solid Films 518 (2010) 2617–2622

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Quantitative analysis of hydrogen in thin films using Time-of-Flight Elastic Recoil Detection Analysis

Zdravko Siketić *, Iva Bogdanović Radović, Milko Jakšić

Institute Ruđer Bošković, P. O. Box 180, 1000 Zagreb, Croatia

ARTICLE INFO

Article history:
Received 9 January 2009
Received in revised form 20 July 2009
Accepted 31 July 2009
Available online 14 August 2009

Keywords:
Hydrogen
Elastic Recoil Detection Analysis
Time-of-Flight

ABSTRACT

Determination of atomic concentrations in thin films is one of the key problems in materials science. Time-of-Flight Elastic Recoil Detection Analysis is a powerful method for depth profiling of light and medium mass elements in near surface layers of material. However, due to poor detection efficiency those spectrometers are not commonly used for hydrogen analysis. We have performed some improvements in order to increase detection efficiency and to make spectrometer more suitable for hydrogen analysis. The spectrometer performance was tested on amorphous Si samples implanted with H^- and D^- and hydrogenised Si standard reference sample. Sensitivity for hydrogen in silicon matrix was found to be several tens of ppm with a surface depth resolution of ~15 nm.

1. Introduction

Hydrogen appears in different materials either as a main constituent (e.g. polymers, organic matter) or as a trace element (e.g. contamination during thin film preparation). Even small fractions of H can have very important effects on the physical, electrical and chemical properties of common metals, semiconductors or insulators.

Analysis of hydrogen in the ppm concentration range and with a depth resolution in the nm range is a great challenge for any analytical technique. Standard elemental analysis techniques such as Auger Electron Spectroscopy or X-Ray Fluorescence can't be used for hydrogen detection. Although very sensitive, hydrogen analysis using infrared or confocal Raman spectroscopy is restricted to a limited number of materials and a selection of molecules containing hydrogen [1,2]. Secondary Ion Mass Spectrometry (SIMS) is a powerful technique for elemental depth profiling with a nm depth resolution. However, method is destructive and quantification of hydrogen is difficult due to high mobility of hydrogen atoms and high background level in SIMS spectrum for low masses [3]. Another available method is neutron elastic recoil detection analysis where 14.1 MeV neutrons were used to depth profile hydrogen concentration in plasma facing components in fusion devices in 100–1000 μm range [4].

Among ion beam analysis (IBA) techniques Elastic Recoil Detection Analysis (ERDA), proton–proton elastic scattering and nuclear reaction analysis are methods that can be applied for hydrogen analysis and depth profiling. The $^1H(^{15}N,\alpha\gamma)^{12}C$ nuclear reaction has been characterized with very good sensitivity and excellent depth resolution [5,6], but such a measurement is time consuming due to the need to tune the incident beam energy to probe different depths in the sample. Sensitivity for hydrogen detection by proton–proton elastic scattering is in the ppm range but depth resolution strongly depends on applied proton energy [7,8].

ERDA with an absorber foil gives information only for the lightest elements (H, He) but no information about heavier constituents in the sample. Also, the depth resolution is significantly worsened by the addition of the stopping foil in front of the semiconductor particle detector. Among more sophisticated systems it is important to mention ERDA with gas ionization chambers [9,10] ΔE–E telescopes with thin transmission ΔE detectors [11] or Ion Induced Electron Emission spectrometers [12]. Also very sophisticated spectrometers like ER using Q3D magnetic spectrograph are used [13]. Such a spectrometer is characterized with sub-nanometer (even monolayer close to the surface) depth resolution for light elements and is used for analysis of ultra thin films.

Time-of-Flight Elastic Recoil Detection Analysis (TOF-ERDA) was developed in mid-1980s by several research groups for applications in different research areas such as optoelectronics, thin-film sensors, interfacial diffusion or reactions semiconductor devices [14–16]. The advantage of TOF-ERDA is that all elements with an atomic mass less than or equal to 28 can be simultaneously detected and depth profiled. Also, the energy straggling due to absorber foils is an order of magnitude smaller than in foil ERDA. The cross-sections for the

* Corresponding author. Tel.: +385 1 456 1012; fax: +385 1 4680 239.
E-mail address: zsiketic@irb.hr (Z. Siketić).

0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.07.196

recoiling of H with heavy ions (Cl, I, Au…) are high due to the mass factor in the Rutherford formula. Therefore, TOF-ERDA spectroscopy is a very sensitive technique for light element detection and analysis.

The reason why TOF-ERDA is not usually used for H detection is that, unlike for silicon particle detectors, the efficiency of carbon-foil time detectors is less than 100% for light elements. The detection efficiency depends on the energy as well as on the electronic stopping power of analyzing recoil atoms in the C foil, and this fact can be particularly critical for hydrogen for which the detection efficiency can drop as low as 10% [17,18]. Therefore, TOF-ERDA spectrometers have not been the best choice for depth profiling and quantification of hydrogen, as can be clearly seen in Ref. [19], where a round robin measurement of H implanted with 6 keV energy in Si is reported. Out of eight involved groups, only one has used TOF-ERDA with carbon foils in timing stations for hydrogen detection without being able to resolve the hydrogen surface peak from the implanted peak.

To improve the relative detector efficiency for the lightest elements, it was important to increase the electron yield from diamond-like carbon (DLC) foils. Thin insulating films are known to be excellent electron emitters. Careful investigation revealed that the yield of ion induced electrons is much larger for insulators than for metals and semiconductors [20,21]. Therefore we coated DLC foils with a thin LiF layer [22]. Using this procedure, Time-of-Flight (TOF) detector efficiency was enhanced up to 60% for 400 keV hydrogen [24] in comparison with other TOF systems where pure thin C foils were used and reported detection efficiency was around 20% [17,25]. In case of TOF-ERDA it is important to have as thin foils as possible to reduce scattering and straggling effects in the foils. The detection efficiency for H comparable to the efficiency reported in the present paper was reported also in Ref. [21,22]. Gujrathi and Bultena [21] report ~90% detection efficiency for 0.5 MeV protons and for TOF-ERDA system with single TOF detector. The Berlin group in Ref [22] state that their detection efficiency for 0.4 MeV protons is 75%. The same group reported in Ref [23] depth resolution for hydrogen near the surface of 10 nm and detection limit of 10 ppm.

To study the capabilities of our TOF-ERDA system for hydrogen measurements, two types of samples were used. To test depth profiling, an amorphous Si (a-Si) sample was implanted with 10 keV H^- and D^- ions. H detection efficiency was tested using an a-Si:H thin-film standard reference material (produced by the Federal Institute for Materials Research and Testing, BAM, Germany) [26]. The effectiveness of the method concerning depth resolution, sensitivity and stability for hydrogen and deuterium analysis are reported.

2. Experimental details

2.1. Samples

A 300 nm thick layer in Si was amorphised (in order to avoid channeling effects) by Si implantation. To obtain a sample containing H, a-Si was implanted with 10 keV H^- ions at nominal fluences of ~1×10^{16} at./cm^2 and ~2×10^{16} at./cm^2. For deuterium depth profiling, we implanted 500 nm amorphous, hydrogenised Si (a-Si:H) with 10 keV D^- ions at nominal fluences of ~1×10^{16} at./cm^2 and ~6×10^{16} at./cm^2. This sample was not used for H implantation due to the very high content of H in the non-implanted sample (9.6 at.%).

The H standard selected to test hydrogen efficiency was a thin layer reference material (a-Si:H BAM standard) with a certified H concentration (12.2 ± 0.5 at.%) and layer thickness (253 ± 10 nm).

2.2. Experimental setup

Measurements were performed using a TOF-ERDA spectrometer developed at the Ruđer Bošković Institute in Zagreb. The spectrometer was installed at a beam line that can accept ions from either a 6 MV EN Tandem (for TOF-ERDA) or a 1.0 MV Tandetron accelerator (for Time-of-Flight Rutherford Backscattering Spectroscopy). All measurements were performed with 20 MeV $^{127}I^{6+}$ ions. The incidence angle toward surface plane was $\theta_{in}=20°$, and the scattering angle between the beam and the TOF-ERDA telescope was $\theta_{scatt.}=37.5°$. During the measurements, the beam current density was kept between 0.03 pnA/mm^2 and 0.1 pnA/mm^2, and the ion beam fluences varied from 0.3×10^{12} particles/mm^2 to 1.6×10^{12} particles/mm^2.

The TOF-ERDA telescope consisted of two timing detectors separated by 523 mm. The particle energy was detected using an ULTRA ion-implanted silicon detector with an area of 300 mm^2. The first timing detector was positioned 478 mm away from the target with a 6 mm collimator placed in front of it to reduce the amount of false start signals. Also, the collimator defined the solid angle of the telescope to be 0.11 msr. The time detectors were electrostatic mirror assemblies using the Busch design [27]. Our assembly included DLC foil (0.4 μg/cm^2 of C grid supported) [28] coated with 2.5 μg/cm^2 LiF, three tungsten grid electrodes and a microchannel plate (MCP) for electron detection. Fig. 1 shows measured values of the dependence of the relative detector efficiency on the electronic stopping power in the LiF. The detailed performance of the TOF-ERDA system as well as the efficiency enhancement for hydrogen is described in Ref. [24]. From Fig. 1, it can be seen that efficiency for ~400 keV hydrogen is ~60% (400 keV is the maximum recoil energy of H in the present measurements).

3. Results and discussion

Fig. 2a) shows typical 2D TOF-ERDA coincidence spectrum. All events belonging to hydrogen isotopes can be extracted and projected to the time axis since the intrinsic energy resolution of the time axis is better than the intrinsic energy resolution of the SB detector [24]. All spectra were normalized to efficiency curve (Fig. 1) while detected H energies were correlated with the depths from which the H atoms emerged. The resulting H depth profiles (directly converted, slab analysis) were compared with profiles calculated by SRIM [29] as well as spectra simulated by the Monte Carlo (MC) simulation code CORTEO [30].

3.1. BAM thin layer reference a-Si:H standard

A measurement of the standard reference material was performed in order to test the measured hydrogen efficiency shown on Fig. 1. Resulting coincidence TOF-ERDA spectrum is displayed on Fig 2a).

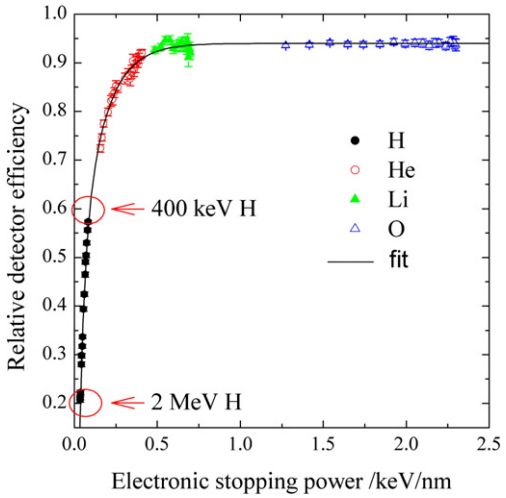

Fig. 1. Relative TOF-ERDA spectrometer efficiency versus electronic stopping power in LiF.