HYDROGEN DETECTION IN SURFACE ANALYSIS: BEST PRACTICES AND STANDARDS

SUMMARY: The quantitative nature of elastic recoil detection analysis (ERDA) complements the superior depth resolution of secondary ion mass spectroscopy (SIMS) for hydrogen detection and depth profiling. Unlike SIMS, ERDA achieves direct quantification of elemental concentrations without reliance on standards based on the fundamental principles of Rutherford scattering cross sections.

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Many alternative energy technologies involve hydrogen generation, transport and storage [1]. Understanding hydrogen-related processes is challenging, as hydrogen's physical properties make it inherently difficult to detect and quantify. There are two groups of ion beam analysis (IBA) methods that allow us to detect hydrogen: (1) high energy elastic or nuclear reaction techniques and (2) secondary-ion mass spectrometry-based techniques. Both produce information about the compositional changes as a function of depth in materials.

ELASTIC RECOIL DETECTION ANALYSIS (ERDA)

ERDA is an accelerator-based IBA method [2]. 2025 will mark the 50th anniversary of ERDA, a technique developed in Canada. ERDA was invented by two groups from the Laboratoire de Physique Nucléaire at Université de Montréal, and the INRS-Énergie in Varennes, Québec [3]. Since that publication, ERDA has proven to be extremely useful for depth profiling of hydrogen and its isotopes in the near-surface region of materials. The high energy accelerator-based method operates by using a MeV-energy ion beam to eject ions from a sample, detecting the recoiled ions to produce a depth profile (Figure 1(a)). Typical ERDA setups either include a stopping foil to filter the projected ions to a solid-state detector or a time-of-flight (TOF) detection system without the stopping foil. Absolute hydrogen quantification is attainable because ERDA is governed by Rutherford cross-sections for

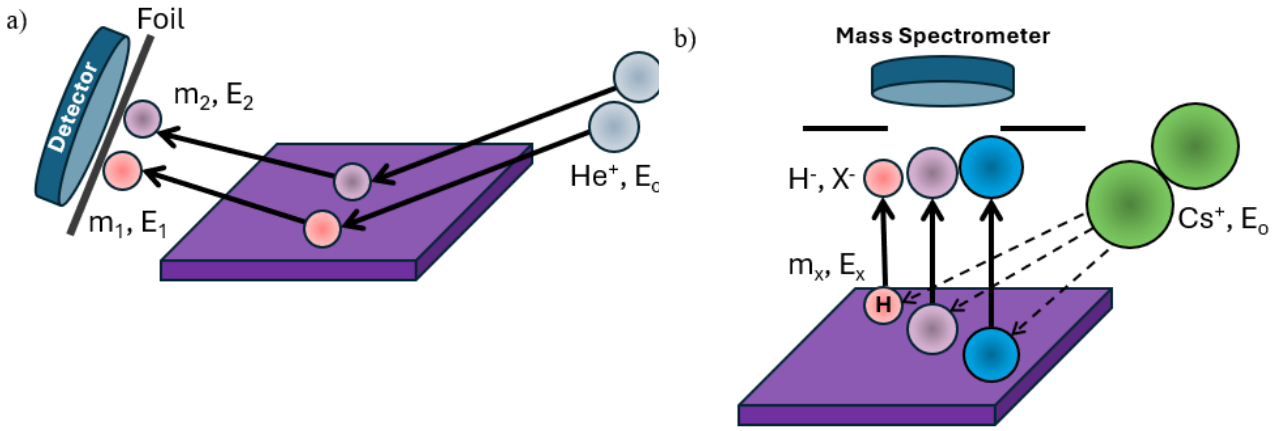

Figure 1. (a) Schematic diagram of ERDA processes. The incident ion (He^+) interacts with the sample and recoils target H^- ions to the detector. The detector measures the energy of the recoiled ions, and the foil filters out incident and other lower in energy ions interfering with the H^- signal, including forward scattered He. E_o is the known incident energy, whereas E_1 represents the detected energy of the recoiled ions. Using E_0 and E_1, a depth profile is constructed; (b) Schematic diagram of D-SIMS processes. The primary ions (Cs^+) sputter the atoms in the impact zone, generating neutral, negative, and positive ions. These secondary ions are separated by a mass spectrometer using the mass-to-charge ratio (m/z). The secondary ions are measured, and the time evolution of the local concentration vs. sputtering time is obtained. To produce a depth profile, additional calculations to convert sputtering time to depth is necessary.

particle scattering (independent of ionization probability), therefore the amount of recoiled hydrogen atoms detected are proportional to that in the sample.

DYNAMIC SECONDARY ION MASS SPECTROMETRY (D-SIMS)

The second group of IBA methods is mass spectrometric techniques including D-SIMS, which can use an accelerator or a keV-energy ion source but at a much lower energy than ERDA. D-SIMS detects hydrogen by analyzing secondary ions sputtered from a surface using an incident beam (Figure 1(b)). Typical setups utilize primary ions of the keV energy range, such as O^+ or Cs^+, to enhance secondary ion yield and achieve precise depth profiling. In SIMS, the incident ion beam sputters the material surface layer by layer, ejecting atoms, molecules, and ions. The secondary ions are detected; and therefore quantification is strongly dependent on the ionization process, which also depends on the composition (matrix effects). While instantaneous intensities can be measured using methods like TOF, one can also plot the temporal evolution of the local concentration to obtain a time profile. The time profile can be converted into a depth profile with the assistance of a profilometry calibration [4].

CALIBRATION STANDARDS

The D-SIMS and ERDA are not without limitations, yet using the techniques together can overcome these challenges. For D-SIMS, quantification is not easily attainable as only a fraction of the atoms

sputtered are ionized. Therefore, the counts measured are not proportional to the sample and a calibration standard of the same composition is needed to account for the ionization probabilities. For ERDA, the sensitivity is not sufficient for ultra-low concentration samples, and it has limited mass resolution for isotopic analysis. Therefore, a goal of this study was to produce ultra-thin film hydrogen calibration standards and depth profile them using D-SIMS and ERDA. D-SIMS offers superior depth resolution and chemical specificity whereas ERDA provides accurate hydrogen quantification. Using the techniques in tandem, each one can make up for the limitations of the other and together provide a complete understanding of hydrogen distribution in a material.

METHODOLOGY AND DISCUSSION

FORMING TITANIUM HYDRIDE

To fabricate hydrogen thin-film hydrogen calibration standards, Si (001) wafers were etched in HF and coated with titanium by magnetron sputter deposition to the thicknesses of 20, 50 and 100 nm. Titanium was chosen because titanium hydride phases are well known, and Ti films have strong adhesion and thickness uniformity on Si.

TiH_x formation was achieved via two methods: (1) gas phase annealing (450°C, 1 hour in a forming gas flow (95% N_2, 5% H_2)) [5]; and (2) galvanostatic polarization (20 minutes at -6 mA/cm^2). In a three-compartment electrochemical cell, the Ti/Si (001) sample was submerged in an electrolyte solution of 0.05 M H_2SO_4 with Ag/AgCl as a reference electrode and Pt as a counter electrode. Cyclic voltammetry (CV) was conducted between -3 V and +3 V. Based on the CV, the optimal current density was determined to be -6 mA/cm^2; more details are given here [6].

MEASURING ERDA SPECTRA

The goal of ERDA is often to measure absolute hydrogen concentration in an unknown sample. When collecting ERDA spectra, the area under the peak (integrated area *IA*) represents the measured yield, or the number of detected recoiled particles (Eq. 1) [7].

$$IA = \Omega Q N_H \sigma(E) \frac{1}{\sin \alpha} \tag{1}$$

This yield is directly related to the areal atomic density (N_H) of the target H atoms. The ion beam fluence (Q) reflects the total number of ions striking the target, while $\sigma(E)$, the energy-dependent cross-section, describes the likelihood of scattering events at a given ion energy. The term $\sin \alpha$ is an angular-dependent geometric correction factor. Quantifying the yield of hydrogen from ERDA spectra enables accurate determination of the hydrogen areal atomic density, linking experimental measurements to the underlying material properties.

BEST PRACTICES FOR ERDA

The TiH_x samples were analyzed using a 2.8 MeV ^{4}He beam in a conventional ERDA setup with an incident angle of 75°, recoil angle of 30° and a 12.3 µm Al-coated mylar range foil in front of the

detector in IBM geometry (incident ion beam and detector in the same scattering plane) [8]. Charge collection was monitored by an intermittent Faraday cup that intercepts the beam in front of the target with a duty cycle of 75%. Kapton® was utilized as a primary standard.

Representative ERDA spectra for Kapton® and TiH_x/Si (001) samples are compared in Figure 2. A Si (001) wafer exposed to air for a short period of time was analyzed to estimate possible surface hydrocarbon contamination. The Stopping Range of Ions in Matter (SIMNRA) program was utilized for fitting ERDA spectra, and the near-surface profile of hydrogen distribution was accurately generated [8]. Exhibiting different characteristics, the TiH_x /Si (001) hydrogen spectrum has a narrow peak, whereas the Kapton spectrum has a lower flattened signal that gradually tapers off. The difference in the shapes is due to the stopping power of the material; TiH_x has a much higher stopping power than Kapton. Furthermore, the intensity of the TiH_x peak can be attributed to a higher density of hydrogen present.

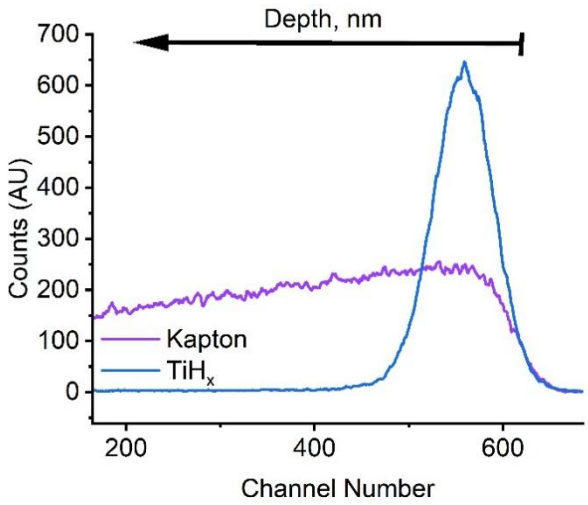

Figure 2. Representative elastic recoil detection spectra for polyoxydiphenylene pyromellitimide (Kapton®) and a 100 nm TiH_x/Si (001) prepared via gas phase annealing.

The TiH_x thin films were analyzed further to assess their efficacy as hydrogen calibration standards. Parameters such as lateral homogeneity, stability over time, and stoichiometries were assessed. To confirm the lateral homogeneity of the hydrogen profile, ERDA measurements were performed on multiple spots of the same sample, separated by at least 1-2 mm. The typical spot-to-spot H peak variation was approximately 2% (calculated from integrated H counts), suggesting a uniform distribution of hydrogen. Additionally, the TiH_x samples were found to be relatively stable over time. Multiple uncertainties are significant for hydrogen quantification (see summary in Table 1). Over a 6-month period, the average integrated H counts for a 100 nm TiH_x sample are ~27 500 and stayed

within 3.8% total uncertainty that is associated with ERDA analysis. All measurements fell within ERDA uncertainties, suggesting stability over time when stored under ambient conditions. Finally, the

TABLE 1

All relevant uncertainties that were considered when calculating the relative uncertainty of the integrated counts measured during ERDA.

Quantity	Description	Relative uncertainty (%)
δIA_H	Uncertainty of integrated area, Poisson statistics	0.6
$\delta\phi$	Uncertainty of recoil angle	0.5
$\delta\alpha$	Uncertainty of sample angle	0.5
δIA_{H_Kapton}	Uncertainty of integrated area, Kapton standard	1.0
δN_{H12}	Spot-to-spot H peak variation	2.0
δI	Ion-beam current integration uncertainty	3.0
Total		3.8

thickness of each layer was calculated with exact stoichiometries determined using SIMNRA. The most prevalent stoichiometries for the annealed samples were $TiH_{1.5}$ and TiH_2, whereas the polarized samples predominantly formed $TiH_{1.7}$.

MEASURING SIMS SPECTRA

Measuring secondary ion intensity (Eq.2) for a particular sample is the quantification principle of D-SIMS. The intensity of secondary ions can be expressed by the following:

$$I_{X+}^{T} = j_p \times A \times Y_{X+}^{T} \times f \times C_{X+}^{T} \qquad (2)$$

where I_{X+}^{T} is the measured ion current of X^+ in the matrix *T*, j_p is the primary ion current density, *A* is the area of analysis, Y_{X+}^{T} is the secondary ion yield in the matrix *T*, *f* is the instrumental transmission factor for X, and C_{X+}^{T} is the atomic concentration of X in the matrix *T*. Secondary ion yield is dependent on the ionization probability, which is strongly influenced by the matrix (chemical environment).

BEST PRACTICES FOR SIMS

D-SIMS was conducted on the TiH_x/Si (001) samples to obtain an elemental depth profile. The samples were analyzed using the Cameca IMS-3f SIMS instrument with the Cs^+ primary beam (40 nA) and secondary ions were detected as negative species. Each analysis area was sputtered in a square of 250×250 µm^2, with the data collected in a 60-µm diameter area in the middle of the sputtered crater to avoid edge effects. Sputtering time was converted to depth (nm) using profilometry, determining

the depth of the crater to be 177 nm. This resulted in a conversion factor of 0.133 nm/s, which is shown on the abscissa of a representative TiH_x/Si (001) D-SIMS spectrum (Figure 3). Note that the Ti signal is higher than the H signal by nearly two orders of magnitude. The ratio between the two signals is not only determined by the difference in concentration of Ti and H in the hydride, but also by the difference in ionization probabilities. Ti, TiH and O signal are persistent at the depth of Si substrate, due to ion intermixing (forward recoils of Ti and O from the top layer), as well as an increase in surface roughness during sputtering processes.

D-SIMS for the TiH_x/Si (001) samples reveal that the hydride is ~60-75 nm thick, as the TiH_x signal decreases in this range, and the Si signal increases. This is expected, as the hydride has a larger volume than the 50 nm of Ti that was deposited on Si (001). Next, there is a large increase of hydrogen on the surface, revealing possible hydrocarbon contamination. TiH^- was also detected as a secondary negative ion to quantify H, as it provides a unique signal related to the TiH_x layer (not affected by H in the vacuum). TiH^- signal drops by an order of magnitude at 80 nm and further goes to 0, indicating no significant H present in the Si substrate. Note that the H (m = 1) signal remains high due to a possible interfering signal from the H-containing species in the vacuum. The interface depth profile shows a complex picture with some layers that can be significant, e.g. SiO_2, visible as a plateau from 60 to 80 nm, and can be related to thin silicon oxide layer that was on the surface prior to Ti metal deposition, while other elements can be due to the ion mixing, e.g. Ti and H can present at the interface due to forward scattering from the layer above.

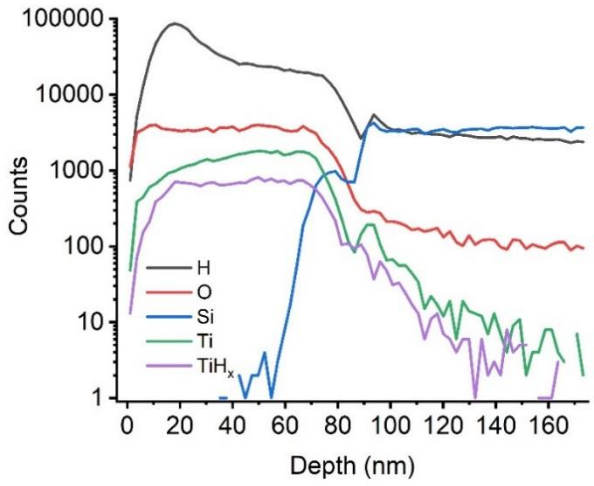

Figure 3. SIMS depth profile for 50 nm TiH_x/Si (001), that was prepared via gas phase annealing, for masses (m = 1(H), m = 16(O), m = 28(Si), m = 48(Ti), and m = 49(TiH)).

SUMMARY

The combination of D-SIMS and ERDA is significant for advancing accurate hydrogen detection in materials science. D-SIMS may be a strong competitor of ERDA due to its superior depth resolution and chemical specificity, but quantification of the results requires the application of ERDA as a complementary technique. This paper reviews a candidate TiH_x/Si (001) standard for hydrogen analysis. It was found to have a uniform hydrogen distribution, long-term stability, and well-defined stoichiometries. The ERDA spectra of the calibration standards provided the quantification of hydrogen's areal atomic density, whereas the D-SIMS spectra provided detailed depth profiles of hydrogen and other associated elements. The information obtained highlights the complementary strengths of ERDA and D-SIMS for comprehensive hydrogen analysis.

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