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I P Jain, A. Jain, P. Jain

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ERDA: Technique for Hydrogen Content and Depth Profile in Thin Film Metal Hydride

I P Jain, **Ankur Jain**, **Pragya Jain**, Centre for Non Conventional Energy Resources, University of Rajasthan, Jaipur-302004, India

Abstract

The use of thin films for hydrogen storage has become very important as the main process of absorption and desorption of hydrogen takes place on the surface of the material. The incorporation of hydrogen into thin film form is relatively new field of research and provides an opportunity to examine a number of unusual properties, which are not visible in the bulk hydrides. Considerable amount of work has been done in our laboratory to investigate hydrogen absorption mechanism in FeTi, LaNi, and $MmNi_{4.5}Al_{0.5}$ thin film metal hydrides.

Over the past few decades thin films are analyzed using ion beam analysis techniques where an energetic incident ion provides depth information on the basis of the energy lost by it and the creation of possible secondary particles in the sample. Rutherford Back Scattering (RBS) technique is based on the principle of elastic scattering of α particles of about a few MeV energy. One of the main drawbacks of RBS is its poor sensitivity for light elements present in a heavier matrix. Hence hydrogen cannot be detected using RBS as backscattering of ions from hydrogen is not possible.

The limitations of RBS are overcome by another technique, Elastic Recoil Detection Analysis (ERDA), in which the yield and energy of particle ejected out of thin film sample under swift heavy ion beam irradiation is detected giving the quantitative information concerning the depth distribution of light elements in a sample. In the present work ERDA technique is being presented with its principle, design, working and application for hydrogen content and depth profile in thin film hydride.

1 Importance of ERDA

- This has become the predominant ion beam technique for quantitative analysis of light elements in thin films.
- The technique is especially for Depth Profiling of light elements overcoming the limitations of RBS, over a wide range of elements from hydrogen to rare earth elements using particle identifying techniques.
- The sensitivity for light elements is enhanced by detecting the recoiled particles instead of the scattered primaries.
- It helps in background free detection of the light elements as different recoiled particles can be identified by their mass or atomic numbers and can be separately counted and measured their energy.
- This is a primary technique for studying content of hydrogen in thin films.
- It has large recoil cross sections with heavy ions and hence good sensitivity and the cross section remains about the same over a wide mass range of atoms.

2 ERDA Technique

In elastic detection (ERD) one determines the yield and energy of particles ejected out of the surface region of samples under MeV ion bombardment, which is an ion beam analysis technique for quantitative analysis of light elements in solids. The sample which has to be analyzed is irradiated with ion beam energy (e.g. O, He, Li, Ag, Au) of several MeV. Light elements (e.g. H, D) from the sample are scattered in forward directions and can be detected with a solid state detector. ERDA makes use of the fact that the information about the target is carried by the target nuclei themselves and not by the backscattered primaries as in RBS which enables us to identify the particles under investigation. Detection in ERDA especially occurs in forward geometry, and therefore, both scattered and recoiled particles will move in the direction of detector.

ERDA was first demonstrated by Ecuyer et al. [1] in 1978 and by Doyle and Peercy [2] in 1979. It is the most frequently used method for hydrogen depth profiling and content measurement in thin films and surfaces [3-5], hydrogen in chemical vapour deposited diamond films [6-7], diamond like carbon films [8-9], plasma deposited amorphous silicon nitride films [10] and in hydrogenated Pb/semiconductor devices [11].

3 Principles of ERDA

In an elastic collision of the incident particle of mass m_p (in atomic mass units) and energy E_p, with the atom of mass m_r (in atomic mass units) present in the sample, the atom in the sample which is at rest, recoils in forward direction after the collision. The energy E_r of the recoiling atom can be derived from the basic principle of conservation of energy and momentum which for atom with mass m_r at an angle ϕ with respect to the beam direction is given by

$$E_r = kE_p, \tag{1}$$

where k is kinematic factor given by

$$k = 4m_p m_r \cos 2\phi /(m_p + m_r)^2 \tag{2}$$

The projectile mass, its energy and recoil angle remains fixed under a given experimental condition, therefore atoms of different masses in the sample come out with different recoil energies as governed by eq. (1). If $m_p > m_r$, projectiles can only be scattered in a limited angular range with a maximum angle ϕ defined by

$$\phi = \arcsin (m_r/m_p)$$

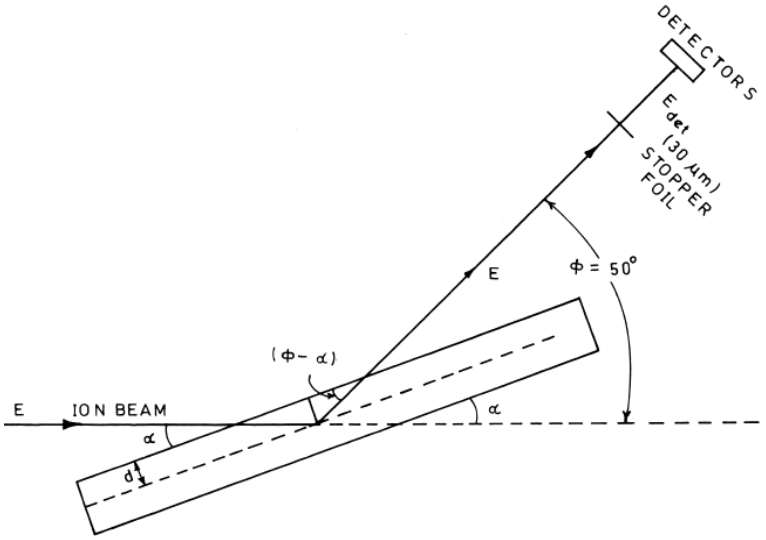

Figure 1: Schematic experimental set up of ERDA indicating path of ion beam and recoil through the sample.

This fact can be used to avoid scattered projectiles by placing the detector for the recoils beyond this angle. Normally the heavier scattered projectiles or recoils of the sample are stopped in a stopper foil of appropriate thickness in front of the detector. Light element recoils are not stopped in the stopper foil due to smaller energy loss during traversal. Figure 1 shows the schematic of an ERDA set up and explains the principle of ERDA.

4 Quantification

The concentration of sample atoms *N*r (in atoms/cm^2) can be determined by the following relation

$$Y_H = N_P N_H \left(\frac{d\sigma}{d\Omega}\right)_R \frac{\Omega}{\sin \alpha} \tag{3}$$

Where hydrogen concentration, N_H is atm/cm^2, N_p is the number of incident ions; Ω is the solid angle subtended by the detector, α is the tilt angle of the sample with respect to ion beam direction and $(d\sigma/d\Omega)_R$ is the Rutherford recoil cross section for H in laboratory frame. The Y_H defined in Eq. (1) is the area under H recoil peak is given by,

$$\left(\frac{d\sigma}{d\Omega}\right)_R = \left[\frac{Z_p Z_t e^2}{2E}\right]\left[1 + \frac{m_p}{m_t}\right]^2 \frac{1}{\cos^3 \phi} \tag{4}$$

Where m_p m_t Z_p and Z_t are the atomic masses and atomic number of the projectile and the target sample respectively, *e* is the electronic charge, E is the incident ion energy and *ϕ* is the recoil angle. It was observed that H concentration decreases during ion irradiation. The H

loss was monitored as a function of dose and was taken into account to evaluate the H concentration in thin films.

5 Depth Profiling

The energy of recoils as detected by the detector depends on kinematics as per eq. (1), energy loss of the incoming ion in the sample up to a certain depth *d*, energy loss of the recoil in the sample from depth *d* where it originates, and energy loss of the recoil atom in the stopper foil.

If the recoil originates from the surface, the energy of the recoil atom is determined only by the kinematics according to eq. (1). This is the maximum energy of recoil of particular mass originating from the sample's surface. The energy of a recoil ion generated at depth *d* is given by

$$E_d = k[E_p - (d/\sin\alpha)(dE/dx)_{in}], \quad (5)$$

where $(dE/dx)_{in}$ is the energy loss of incoming ion in the sample material.

The energy of recoil E_{ds}, originating at depth *d*, coming out at the surface is

$$E_{ds} = E_d - \{d/\sin(\phi-\alpha)\}(dE/dx)_{out}, \quad (6)$$

where $(dE/dx)_{out}$ is the energy loss of recoil in the sample. The recoil energy as detected by the detector is given by

$$E_{det} = E_{ds} - \Delta E_{foil}(E_{ds}), \quad (7)$$

where ΔE_{foil} is the energy loss of recoil in the foil, which is dependent on energy. The recoil energy is converted to depth scale using the eqs. (5) to (7) given above.

6 Mass Identification

Recoil energy provides the information about the mass of the elements in the sample as per eq. (1) at fixed ϕ. The identification of the elements from the recoil energy is possible as long as the recoil energy difference of the elements is larger than the energy resolution of the set up. Higher mass recoils have higher energy as per eq. (1), if $m_p > m_r$ and appear as separate groups.

7 Sensitivity

Sensitivity is defined as the minimum quantity of an element, which can be detected for a moderate charge of incident ions (say 10 μC). It is dependent on the recoil cross section and the detector solid angle. The latter is kept normally in such a way that the opening of detector has an acceptance angle, which is comparable or smaller than the kinematic broadening. Typically, the minimum detection limit is about 0.1 atomic per cent.

8 Depth Resolution

Depth resolution depends on the energy resolution d*E*, which is governed by various factors such as, incident ion beam energy spread, straggling in the stopper foil and the detector system, inhomogeneities in the stopper foil and the entrance window of the detector, detection system resolution, which is composed of the electronics noise and the detector resolution, kinematic broadening and angular and lateral spread due to multiple scattering, which adds to the kinematic broadening. Incident beam resolution is typically 50 keV. Detection system resolution is typically 1% and is therefore about 200 keV for 20 MeV heavy ion recoils. One has to choose the experimental parameters in such a way that the recoil energy spread due to various factors is minimized.

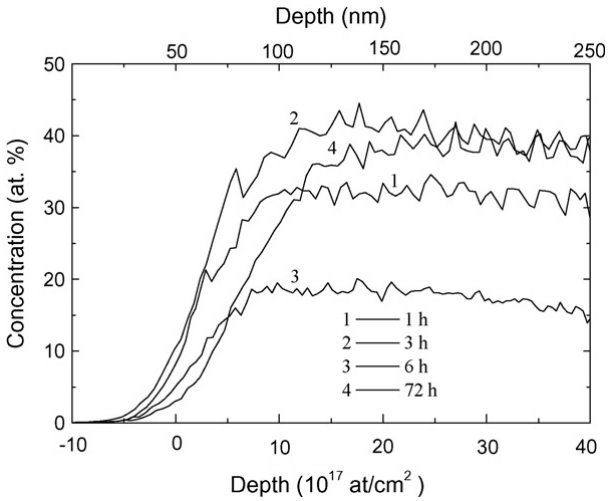

Figure 2: Hydrogen distribution profiles in MgNi films at 250 8C [13].

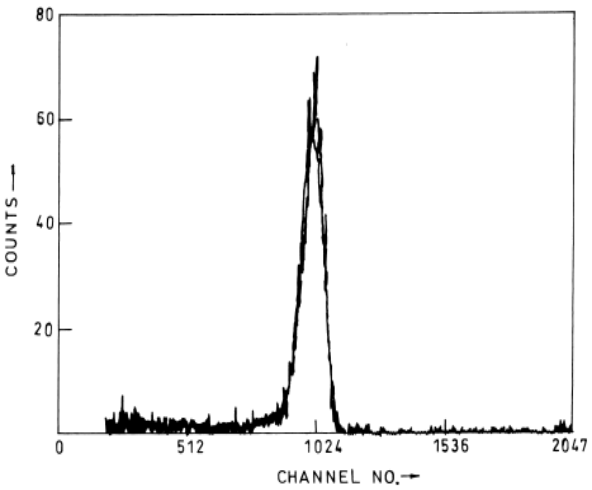

Figure 3: Hydrogen content in hydrogen loaded FeTi thin films [15].

9 Hydrogen Depth Profiling

The hydrogen content has a great influence on the chemical, physical and electrical properties of many materials. Therefore, it is necessary to monitor the H-concentration by depth profiling. Wielunski et al [12] has compared the hydrogen depth resolution in multilayered metal structure (Al/Cu/Ag/Au) by ERDA and NRA techniques. Pranevicius et al. [13] investigated the Hydrogen distribution profiles in Mg-Ni films (Figure 2). Wirth et al. [14] studied the changes in surface barrier layer of Mg-Ni films by hydrogen profile. Hydrogen concentration in unloaded and hydrogen loaded FeTi thin films were measured by Jain et al [15] by ERDA with 160MeV Ag ^{107} ions and found that hydrogenation of the films increased the H-content by a factor of 5-10 atm% (Figure 3).

10 Conclusions

ERDA technique is important as it provides the yield and energy of particle ejected out of thin film sample under swift heavy ion beam irradiation giving the quantitative information concerning the depth distribution of light elements in a sample with 1nm resolution. ERDA is already a very useful technique having good sensitivity and high resolution, but it needs to be

further improved. It has the excellent capability for fast quantitative concentration depth profiling of elements and capable of giving the total abundances of light elements in surface layers. It is an important technique which helps in our understanding of hydrogen content and its depth profile in a thin film samples, which is very important for the hydrogen storage in various materials for ultimately solving world's energy problem. In our laboratory lot of work is being done and is under progress using ERDA to understand the actual hydrogen absorption mechanism in alloys and compounds.

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