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ELASTIC RECOIL DETECTION ANALYSIS (ERDA) OF ION IRRADIATED POLYMERS

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ABSTRACT

Elastic recoil detection analysis (ERDA) is used in the forward recoil spectrometry to measure the hydrogen content in hydrogenated polymers like polyethylene (PE) and polystyrene (PS) thin films.

Detecting the recoil hydrogen atoms due to impinging 2.0 MeV helium ions one can measure the hydrogen concentration in the film and the amount of its isotopes.

Results demonstrate that bombarding these polymers and increasing the ion fluence the hydrogen concentration decreases, due to a strong hydrogen outgassing during ion irradiation, as typical trend of many polymers. At high ion fluence the polymer evolves to a carbon rich material changing drastically its physical and chemical properties.

1. - INTRODUCTION

Atoms ionization produced by the higher energy ion deposition in polymers makes a profound change in the final product of the reaction. 1.0 MeV He^+ ion, for example, ionizes about an atom in each atomic layer it penetrates so it is possible to product particular chemical reactions along its ion track. Radiation effects induced by light impinging ions have been largely used to modify the chemical and physical properties of polymers(1,2).

When polyethylene, polystyrene and polymethylmetacrylate polymers are ion bombarded the dominant induced reaction is a strong break up of chemical bonds in the chains resulting in a large hydrogen emission leaving to a carbon enriched material. These effects are confined to a cylinder around the ion track with a cross section of the order of 10^{-15} cm^2 and with a length comparable with the ion range(3,4).

To investigate on this subject the forward recoil spectrometry was used. This ion beam analysis technique, which is alternative to specific nuclear reactions, can be used, in fact, to detect hydrogen and to measure film thicknesses and depth profiles of hydrogenated polymers. It is particularly attractive because of its excellent high sensitivity, which is approximately 0.1 atomic percent hydrogen or deuterium, and depth resolution, which is about 500 Å (5,6,7).

In combination with the detection of backscattered ions (RBS) or nuclear analysis (NRA), one can determine the depth distribution for most atomic components of the sample in a measurement of some minutes. The present paper wishes to discuss on ERDA techniques in application to dehydrogenation of polymers during MeV ion irradiation.

2. - FUNDAMENTALS OF ION BEAM ANALYSIS

In the ERDA experiment, a monoenergetic He^+ beam of energy E_0 is directed toward a sample at an o incidence angle with respect to the sample surface, as shown in the experimental set up of Fig.1.

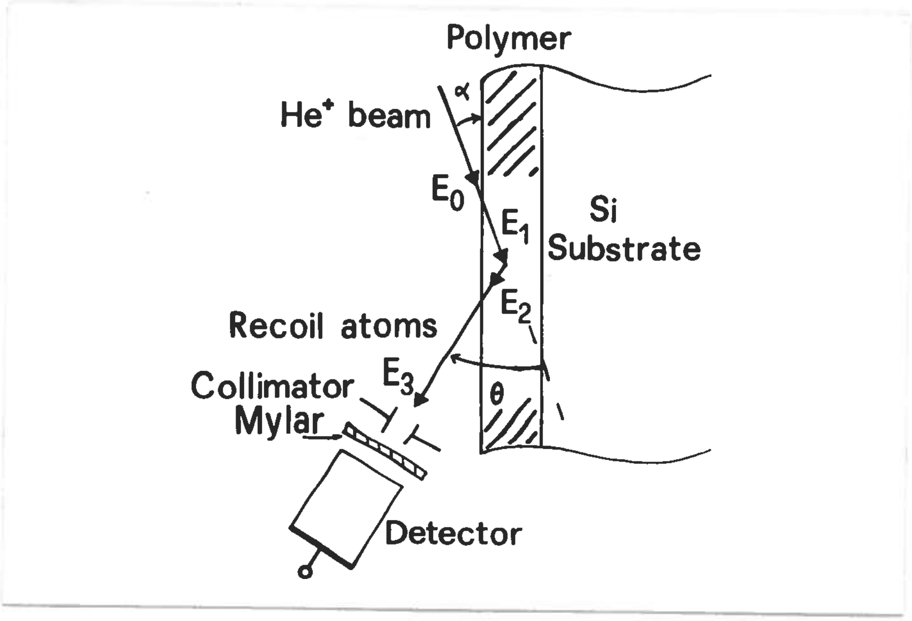

Fig.1: Geometry and experimental set-up of the forward recoil spectrometry.

The subsequent collision of the ion beam with the target nuclei may result in the ejection of those nuclei with energy E_2, proportional to the incident beam energy E_1 just before impact, according the relationship:

$$E_2 = K\,E_1 \; ; \qquad (1)$$

where K is the "kinematic factor" for the scattering, which is given by:

$$K = [4M_1M_2/(M_1+M_2)^2] \cos^2\theta. \qquad (2)$$

Here M_1 and M_2 are the masses of the helium projectiles and of the target nuclei respectively and θ is the recoil detection angle. At $\theta = 30°$ the kinematic factor is 0.48 and 0.67 for hydrogen and deuterium nuclei, respectively.

The number of nuclei that recoil from a particular depth within the sample will depend on the area density of nuclei at that depth. The n(E) energy spectrum of the detected recoils is given by the following relationship:

$$n(E)dE = N\Omega\ \sigma(E_1)C(x)dx; \qquad (3)$$

here N is the number of incident particles, Ω is the solid angle of detection, $\sigma(E_1)$ is the elastic scattering cross-section, C(x) is the concentration profile of hydrogen at the x depth and dE represents the energy width of a single channel (KeV/channel) corresponding to the energy loss in the dx sample layer.

A mylar foil is placed in front of the semiconductor detector to stop the forward scattered helium projectiles and heavier nuclei. The recoiling particles, which are less massive and thus travel at higher velocities, pass through the filter with a modest loss in energy. It follows from the above discussion that the energy of a detected particle is:

$$E_d = E_3 - \Delta E_s; \qquad (4)$$

where E_3 is the energy which a recoiling nuclei has after leaving the sample surface and ΔE_s is the energy which is loses while passing through the stopper foil. If we consider the case where both hydrogen and deuterium are on the sample surface, since $E_3 = E_2 = KE_o$, then:

$$E_d = KE_o - \Delta E_s; \qquad (5)$$

Alternatively, if the particle is located at a depth x beneath the sample surface then:

$$E_3 = [E_o - S_1 x/\sin\alpha]K - S_2 x/\sin(\theta-\alpha); \qquad (6)$$

here S_1 and S_2 are the energy loss rates (dE/dx) for the incident helium ion and the recoiling hydrogen nuclei respectively. The term $S_1x/\sin\alpha$ is the energy that the helium loses after travelling to a distance x below the surface. The term $S_2x/\sin(\theta-\alpha)$ is the energy that the recoiling particle loses on its way out of the sample. It follows that:

$$E_d = KE_o - [S]x - \Delta E_s; \qquad (7)$$

where $[S] = KS_1/\sin\alpha + S_2/\sin(\theta-\alpha)$ is the so called "energy loss factor".

The energy loss functions of hydrogen and deuterium in the stopper foil are experimentally determined by measuring the energies at which they recoil from the polymer film as a function of E_o. The spectra energy scale is then converted to a depth scale by using the tabulated energy stopping powers(8) to find S_1 and S_2.

Finally, one obtains the depth profile in the polymer films by dividing the spectrum height of recoiled hydrogen from the samples with that of a standard sample. This procedure permits to detect together hydrogen and deuterium since the energy loss rates of helium beam, hydrogen and deuterium recoil particles are the same in deutered and in hydrogenated polymer films.

The depth resolution, which is the ratio between the total energy spread and the energy loss factor, near the surface is very good (about 500 Å) but in deeper regions became poor.

3. - EXPERIMENTAL METHODS

The analysed samples are thin polymeric films supported by a polished silicon backing. The film thicknesses, ranging between 0.02 to 2 μm, were measured in the polymer-substrate edge before each ion irradiation by using a Talystep Sistem with a depth resolution of 100 Å.

Each film was produced by spinning a polymer solution onto a silicon slide for times of the order of 30 sec and velocities of about 4000 tours per minute. By changing the polymer solution concentration, in chloroform solvent (~ 1 gr/25 cc), the film thickness was changed from 500 Å up to 2 μm.

PS spinned films with and without deuterium were analysed with 2.0 MeV helium beam before and after different ion fluences going from 10^{15} to 5×10^{16} ion/cm^2. The helium ions hit the sample surface at an angle of incidence of $\alpha=15°$. The used current densities were of the order of 10 nA/mm^2, the spot was 6 mm^2 and the chamber vacuum was 10^{-6} mbar. The helium dose was of $2\text{x}10^{15}/\text{cm}^2$ for each ERDA analysis.

The energy of the recoiling particles was measured using a silicon surface barrier detector which is located at an angle of $\theta=30°$ behind a filter of 10 μm mylar film. A collimator 1x3 mm was placed in front of the detector to increase the energy resolution of the acquired spectra. Experimental solid angle subtended by the detector was about 1 msr. All the measurements were executed at room temperature. When a particle is detected, a current pulse proportional to the particle energy is produced. The magnitude of this signal is measured and monitored as "counts" through a multichannel analyzer (MCA).

Fig.2 shows two typical ERDA spectra of PS films, 1000 Å thick and 50% deutered the first (a) and 1.5 μm thick and 100% deutered the second one (b). Shown here are two well defined peaks; the lower energy peak is due to hydrogen in the hydrogen-deutered-PS film and the higher energy peak is due to the deuterium in the d-PS sample.

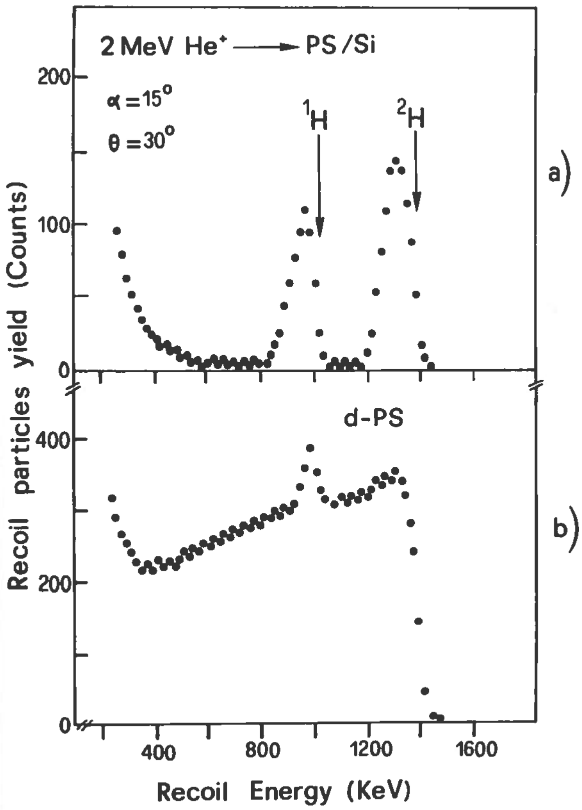

Fig.2: ERDA spectra of hydrogen and deuterium from 1000 A PS film 50% deutered (a) and 1.5 μm PS film 100% deutered (b). Spectra were acquired using 2 MeV helium beam and 10 μC charge.

In this experiment the energies of the hydrogen and deuterium recoiling from the surface are of 960 KeV and 1333 KeV, respectively. The energy loss of these particles in the mylar filter is of about 230 KeV. Since the energy of deuterium from the surface is higher than hydrogen one must avoid making the d-PS film too thick so that the deuterium recoiling from deep does not overlap in energy with the hydrogen recoiling from the sample surface. Fig.2b shows this overlap for a hydrogen peak due to surface contamination of the deutered PS film. The peaks and edges of the spectra are broadened due to the finite resolution of the instrumentation, which is approximately 40 KeV. This energy resolution limit corresponds to a depth resolution Δx of 380 Å at the sample surface and of about 700 Å at 5000 Å depth. For the used geometry the energy, and thus the depth, resolution is controlled primarily by the detector resolution and the straggling of the recoiling nuclei through the mylar foil.

The concentration profile of hydrogen contained in the PS (or PE) pre-bombarded films has been obtained from the ratio between the signal height in the energy ERDA spectra, obtained in the same experimental analytical conditions, of a standard sample of PS (or PE) bulk analysed with a very low helium dose (2×10^{15} ion/cm^2) and that of the sample film. To analyse the carbon concentration in the polymer film we have used the protons backscattering spectrometry (PBS). The elastic scattering of protons, according the $^{12}C(p,p)^{12}C$ reaction, can be used, in fact, to measure the target carbon content detecting the proton scattering at 165° angle with respect to the beam direction, which has high cross section values at proton energies ranging between 500-1800 KeV(9).

4. - RESULTS

To calibrate the forward recoil technique, measurements on hydrogen concentration in polymer films have been tested with commercial thick standard samples where the stoichiometry (hydrogen/carbon ratio) is well known: polystyrene (C:H=1:1) and polyethylene (C:H=1:2) thick films.

Ion irradiation of thin polymer films, at ion doses of the order of 10^{16} ion/cm^2, shows a preferential loss of hydrogen and the depth profile indicates that the hydrogen depletion is almost uniform in the entire bombarded film.

Fig.3, for example, shows the comparison between three spectra of recoil hydrogen yielded from 1.5 µm PE films: just spinned on a silicon substrate and after an ion fluence of 6×10^{15} ion/cm^2 of 2.0 MeV proton and helium beam irradiations. Hydrogen content decrease going from starting film (as deposited) to proton and helium irradiated ones testifying a strong target outgassing versus ion fluence.

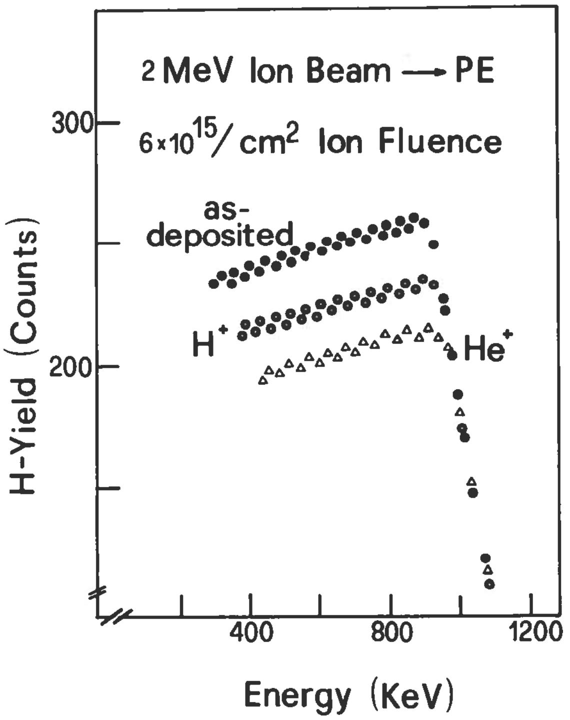

Fig.3: Comparison between three hydrogen recoil spectra from 1.5 µm PE film: as deposited on Si substrate and after an ion fluence of 6×10^{15} ion/cm^2 of 2 MeV proton and helium beams.

The change in hydrogen concentration of irradiated PE films is reported in Fig.4. Upper section (a) shows the percentage hydrogen loss measured versus ion fluence for 2 MeV proton and helium irradiation. Low section (b), instead, shows the hydrogen concentration as function of the ion fluence for different irradiated polymers.

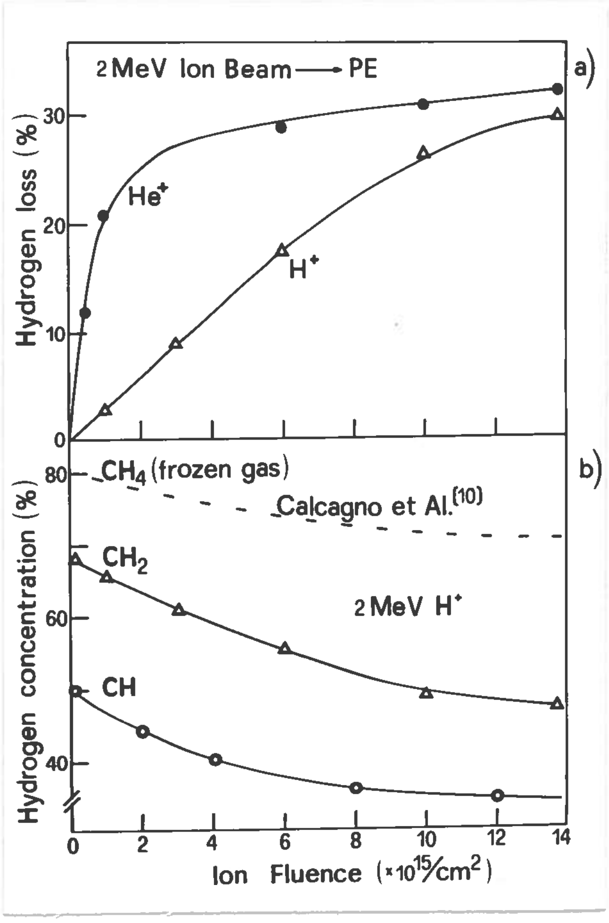

Fig.4: Percentage of hydrogen loss as a funcion of the ion fluence for 2 MeV proton and helium irradiation (a) and comparison between the hydrogen concentration decrement versus the ion fluence for different idrogenated polymers (b).

Experimental data give an exponential trend with the ion fluence indicating a decrement of the hydrogen concentration of the order of 30% of its initial value at ion fluence of about $10^{16}/cm^2$. The dehydrogenation efficiency is high for helium beam compared to the hydrogen one indicating that this phenomenon can be dependent by the particle energy stopping.

Similar results, investigated with other tecniques, have been obtained in polystyrene, polypropylene and frozen methane (4K) films deposited on Si substrate by Calcagno et Al.(10).

Our results indicate that the H_2 emission yield, in bulk polymers, is of the order of 10^4 mols/ion, according literature data obtained by using the mass quadrupole spectrometry to detect the hydrogen emission during the ion beam irradiation(4,11). This value became about a factor ten higher by using an irradiation with heavy ions (100 KeV N^+ or Ar^+). Then, increasing the incoming particle energy stopping the hydrogen release became very fast and the residue carbon films are obtainable with little fluences.

The measures concerning the carbon concentration in polymers versus ion fluence, by using the PBS technique, indicate that during the ion irradiation the carbon concentration remain constant. Then, the C/H ratio increases with the ion fluence rise due only to the polymer dehydrogenation effect.

5. - CONCLUSIONS

Though nuclear reactions , like $^{1}H(^{15}N,\alpha\gamma)^{12}C$ or $^{1}H(^{19}F,\alpha\gamma)^{16}O$ are high sensible to detect hydrogen and its isotopes, the need to use heavy ion beams at high energy of 6.4 and 16.5 MeV, respectively, limits the analysis performance to few laboratories. The elastic recoil detection analysis with light ion beams at 1-3 MeV energy is a very promising technique to analyse hydrogen profiling in solids by using a conventional Van de Graaf accelerator.

In polymers ERDA analysis has been applied with successful because its simplicity, good resolution (~400-700 Å) and sensitivity (~0.1 at.%).

In respect to other ion beam techniques, ERDA offers the following advantage:

- a low energy accelerator with conventional equipment used for RBS analysis is required;
- can be simultaneously detected hydrogen and its isotopes;
- the need data collection time is short (10-30 min);
- the depth resolution and the depth scale can be easily adjusted according to the type of the analysed sample changing the angles α and θ.

Results demonstrate that ion bombardment of hydrogenated polymers at high fluence produces strong hydrogen outgassing changing their properties. Ion irradiated polymers exhibit, in fact, a variation in their chemical and physical properties. It was obtained, for example, that ion bombardment of polymers tend to increase the relative carbon content of the material so the colour of polymer film change toward black modifying its electric conductibility, as studied by Venkatesan et Al.(12). Increasing the ion fluence the polymer density increases and its solubility is reduced indicating a cross link of the chemical bonds(13).

By using ion irradiation in nuclear and electronic energy loss regimes and at doses of the order of $10^{16}/cm^2$ the dehydrogenation process and the consequent film carbonization is quite general and typical of many polymers. The hydrogen outgassing in irradiated polymers are due to the dissociation ion induced along the ion track that produces the breakup of a large number of bonds in the main chain of the material. The region interested by this phenomenon per single ion has a cross section of the order of 10^{-15} cm^2 and a length equal to the ion range, according literature(12). The ion beam interaction with

PE and PS material gives a cumulative effect of individual ion tracks in agreement with the exponential trend of the hydrogen concentration as a function of ion fluence.

Finally, results demonstrate that the yield of hydrogen release is proportional to the ion stopping power and than the energy deposited along the ion track is the key parameter of the investigated process. These investigated radiation effects can be understood by using as analysis tecnique the forward recoil spectrometry.

RIASSUNTO

L'analisi della rivelazione del rinculo elastico (ERDA) di atomi di idrogeno indotto da ioni elio di 2.0 MeV di energia è stata adoperata per misurare il contenuto di idrogeno di sottili film di polimero, come polietilene (PE) e polistirene (PS).

Questa tecnica di analisi, alternativa alle reazioni nucleari, rappresenta un metodo rapido e non distruttivo per determinare simultaneamente la distribuzione in profondità degli isotopi dell'idrogeno presenti in una matrice pesante.

I risultati ottenuti dimostrano che la concentrazione di idrogeno nel polimero decresce all'aumentare della dose degli ioni incidenti poichè la deposizione di energia lungo la traccia dello ione libera idrogeno. Questa caratteristica mostrata da molti polimeri idrogenati porta, ad alte dosi, alla formazione di un materiale ricco in carbonio e ad un cambiamento delle sue proprietà fisico-chimiche.

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