Producing and characterization of thin films of ternary and quaternary systems: W/C/Mg/O/N)
Small band-gap nanostructured perovskite materials for photovoltaic and photocatalytic hydrogen generation applications

D. Pantelica[1], P.Ionescu[1], H. Petrascu[1], C.Nita[1], Maria Dinescu[2]

[1]*Horia Hulubei National Institute for Physics and Nuclear Engineering (IFIN-HH), P.O.B. MG-6, RO-077125, 30 Reactorului St., Magurele, ROMANIA*

[2] *National Institute for Laser, Plasma and Radiation Physics, 409 Atomistilor Str., RO077125, Magurele-Bucharest, ROMANIA*

We intend to perform investigation by IBA techniques (RBS, NRBS, ERDA) of thin films of W/C/Mg with different N_2 and/or O_2 contents. The layers will be deposited by Pulsed Laser Deposition assisted by RF discharge in oxygen, nitrogen or a mixture between the two gases. As substrate Eurocer will be used; this is the main material of ITER Tokamak components (torus internal wall, etc.). The obtained experimental data will be used, together with other characterization results as XRD, AFM, SEM, spectroellipsometry for reports in the frame of the **European Project EURATOM WP12-IPH-A01-2-02 / BS-21** „*Producing and characterization of thin films of ternary and quaternary systems: W/C/Mg/O/N",* (2013)

Also, we intend to perform characterization by IBA techniques (RBS, NRBS, ERDA) of $LaTiO_{3-x}N_x$, $BiFeO_3$, $YSiO_2N$ and $YGeO_2N$ thin films deposited by radiofrequency assisted reactive pulsed laser deposition. The investigations goals will be the chemical analysis of the layers (stoichiometry identification) and thickness evaluation. The obtained experimental data will be used, together with other characterization results as XRD, AFM, SEM, ferroelectric hysteresis measurements, spectroellipsometry, for reports in the frame of. NRSRP 2011 – 2016 Romanian-Swiss Research Programme, No. **IZERZO-**

142176/1 *Small band-gap nanostructured perovskite materials for photovoltaic and photocatalytic hydrogen generation applications",*(2013-2015).

Rutherford backscattering spectrometry with light ions, typically 1–2 MeV ^{1}H or ^{4}He ions, is a often used technique for depth profiling of elements concentrations. Furthermore, under channeling conditions, the technique may be exploited to give information about the sample structure and lattice locations of impurities. Channeling is a powerful technique which is widely used for ordered samples characterization.

In the extensive use of elastic backscattering for materials characterization purposes, ^{4}He particles up to several MeV have been for long considered as most convenient projectile. This often gives sufficient mass and depth resolution. However, the case of more complex film structures, with compound materials, have put higher demands on both the mass and the depth resolution in the analysis.

The RBS technique has also its limitations. Mass resolution for heavy elements and sensitivity for light elements are poor, and, except for the surface, mass determination is not unambiguously possible. The analysis of light elements in a heavier matrix is often impossible, because of the energy overlap of the beam ions scattered by light surface atoms and by heavier bulk atoms deeper in the sample. Furthermore, small amounts of light elements are difficult to analyze, because of the Z^2 dependence of the Rutherford cross section.

It is well known that the mass and depth resolution, as well as the sensitivity may be improved by using heavier and more energetic ions. In particular, mass separation for medium and heavy elements is improved significantly by heavy ions RBS. The expression for the energy separation as a function of the projectile mass M_1, the projectile energy E_0 and the target mass M_2 can be written as:

$$\Delta E \cong \frac{2M_1E_0}{M_2^2}\left(1-\cos\theta\right) \quad (1)$$

where θ is the backscattering angle. This is valid for $M_1/M_2 << 1$. The expression suggests the use of higher mass projectiles and higher bombarding energies. There are, however, some drawbacks, because the resolution of the silicon detector is worsened and, due to $1/E_0^2$ dependency of the cross section, the counting rate reduces. Subsequently, longer analyzing time has to be used if higher energies are needed. In order to avoid the worsened resolution of silicon detectors for heavy ions the measurement of backscattered ions energy using a time of flight spectrometer can be used.

A severe disadvantage of conventional RBS is low sensitivity for light elements. The Rutherford scattering cross section is proportional to the square of the nuclear charge of the target nucleus. Therefore, the scattering peaks from light elements such as C, N and O are superimposed on a relatively high background due to backscattering from heavy elements in the sample. In recent years, high energy ^{1}H and ^{4}H backscattering has been utilized to overcome this difficulty and to quantify the stoichiometry or to profile the light elements in the heavy bulk samples. In the high energy backscattering experiments, ^{1}H and ^{4}He ions of *3–9 MeV* (or even more) are used as incident projectiles. The elastic scattering cross section for light elements becomes a

nuclear rather than a Rutherford interaction, called non–Rutherford backscattering or nuclear resonance elastic scattering. The non–Rutherford backscattering can be used to enhance the sensitivity for light elements. For example, at ^{4}He energies of *3.045*, *4.265* and *3.72 MeV* the elastic backscattering cross sections for O, C and N are 25, 150 and 6 times larger than their corresponding Rutherford cross sections, respectively.

We intend to use RBS and NRA techniques to characterize the thin layers of the above mentioned materials. Both RBS and NRBS with ^{4}He will be used. The measurements will be performed using a dedicated target chamber. The experiments will be performed at the 3 MV Tandetron accelerator using a standard backscattering setup. The energy of the ^{4}He beam used for measuremens will be calibrated. The method adopted for calibration of the Tandetron accelerator consists simply of comparing the energies of alpha particles from a radioactive source with the energies of ^{4}He projectiles back-scattered into an silicon detector by thin carbon and gold layers.

The ions scattered at 165^0 will be detected by a Si detector having 15 keV resolution.

A possibility to characterize light elements is to perform elastic recoil detection analysis (ERDA) with high energy heavy ions, which allows the simultaneous measurement of a wide range of elements, including hydrogen [1]. The first use of a (ΔE - E_r) ionization chamber in elastic recoil detection measurements was reported in [2]. In IFIN at the Nuclear Physics Department we started almost 18 years ago to use our 9 MV tandem accelerator for material analysis . An ERDA beam line equipped with a dedicated target chamber has been installed. A compact ΔE - E_r telescope (Fig. 1) consisting of a gas (ΔE) ionization chamber and a silicon (E_r) detector has been developed.

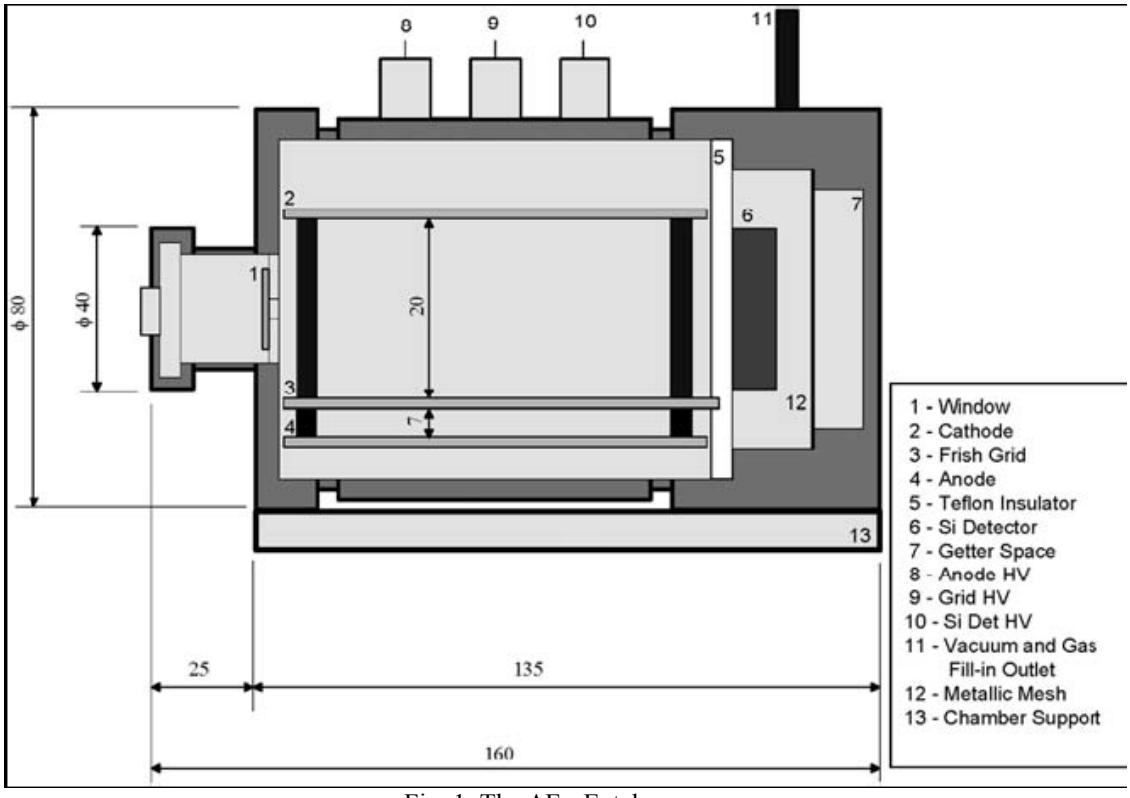

Fig. 1. The ΔE - E_r telescope

A prerequisite for the precise quantitative evaluation of the ERDA data is the correct energy calibration of the data. The data acquisition system is used to register all multiparametric events during the experiment; data are registered in list mode on disk for further processing. The total two-parameter (ΔE-Er) spectra are reconstructed after the experiment. For each element present in the sample, the total energy spectrum (histogram) was built using the PAW program. However, to reconstruct the total energy spectrum, the energy calibration for both the ionization chamber and the Si detector should be determined. An example of our data for one of the runs is shown in Fig. 2, in the form of calculated energy versus measured pulse-height. The lines represent the best fit with a second order polynomial to the data points.

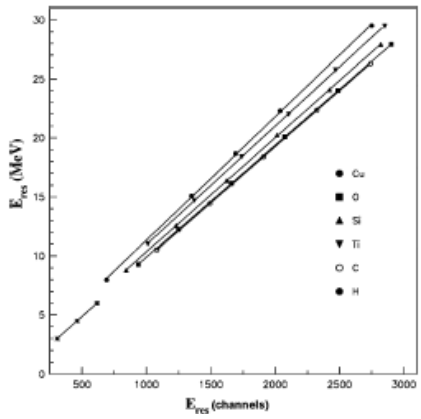

Fig. 2. Calibration curves energy versus pulse height measured for the Si detector.

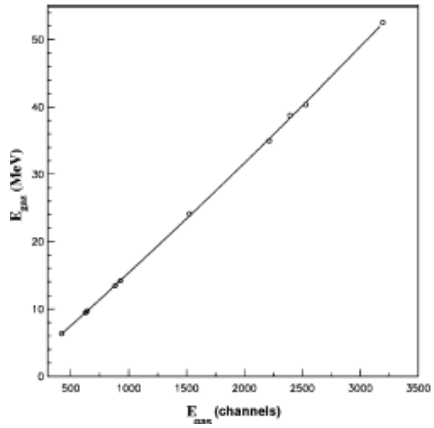

Fig. 3. Calibration curve (energy versus pulse height amplitude) measured for the ionization chamber.

The slope increases systematically from light to heavy ions. The PHD increases with increasing ion energy and charge. For our detector the PHD is considerable, even for relatively light ions like ^{12}C, ^{16}O and ^{28}Si. For the same ions elastically scattered from the Au foil we measured two parameter ΔE - E_r spectra at different gas pressures and ion energies. Using calculated energies for the elastically scattered ions, corrected for energy loss in the gold foil and in the mylar window, we get the total energy of the ions when entering the ionization chamber. The residual energy E_r can be determined using the calibration curves measured for different ions. The difference between the total energy and residual energy represents the energy loss in the gas. So, an energy calibration of the ionization chamber can be accomplished. In Fig. 3 we present the calibration data for the ionization chamber, measured in one of the runs.

The procedure followed to extract the information about the composition of a sample form experimental data taken in ERDA measurements consists in three steps:

– getting the calibration coefficients from calibration runs;

– build the total experimental energy spectra (histograms) for each sample, and for each element present in the sample (Fig. 4);

– adjust the parameters describing the sample composition so that the theoretical spectra reproduce the experimental ones(Fig. 5).

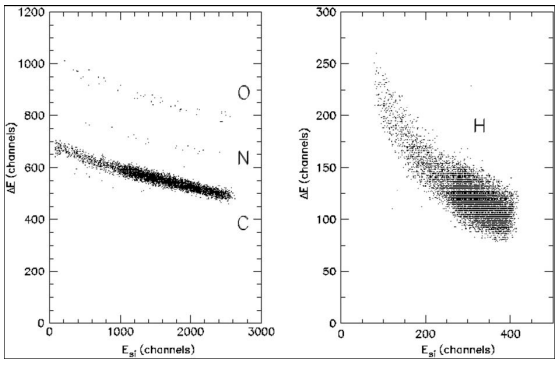

Fig. 4. ΔE - E_r spectra measured with a 63Cu beam at 80 MeV incident on a DLC sample.

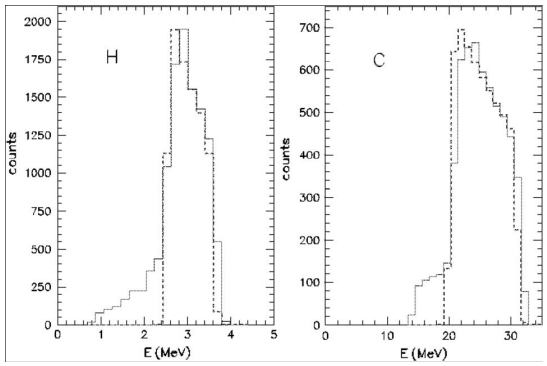

Fig. 5. Total energy spectra of the main components of the DLC sample.

Fig. 6 shows the ΔE - E_r spectra corresponding to high and normal amplification of a $MgAl_2O_4$ single crystal sample implanted with 30 keV He ions at a fluence of $2x10^{16}$ at/cm^2. The spectra were taken with a 80 MeV ^{63}Cu beam. The H recoils from the sample surface and He recoils are seen in the identification matrix corresponding to high amplification of the ΔE signal. The identification matrix corresponding to normal amplification shows O, Mg and Al, the components of the spinel. Because the surface of the sample was covered with a thin carbon layer in order to avoid charging effects, the carbon signal from the surface is also present.

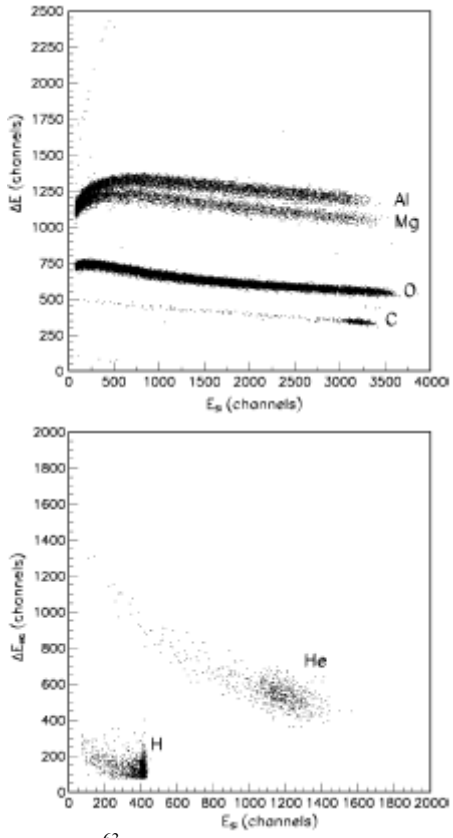

Fig. 6. ΔE - E_r spectra measured with a ^{63}Cu beam incident on a $MgAl_2O_4$ single crystal implanted with 30 keV He ions at a fluence of 2 $x10^{16}$ at/cm^2

We will use the ΔE - E_r telescope from the 4th beam line. The electronic set-up which will be use is fairly conventional. The energy loss signals and the residual energy

signal will fed to three ADCs that were parts of a multiparameter acquisition system based on a PC, where the data will be stored.
Bem request:
- 6 days (18 shifts) at the 3 MV Tandetron accelerator
- 6 days (18 shifts) at the 9 MV Tandem accelerator

References

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