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Received 11 February 2005, accepted 12 April 2005

The application of nuclear analytical methods on surface and interface study is presented. Two topics are included in the presentation - polymer-metal interaction studies and study of single-crystalline structures using RBS-channeling method. Diffusion of Ag atoms in polyethyleneterephthalate (PET) was studied using Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection Analysis (ERDA). The samples were prepared by deposition of Ag thin layers on polymer surface using CVD and diode sputtering techniques. Faster diffusion of Ag atoms was observed from non-compact Ag layers prepared by diode sputtering than from those prepared by CVD technique. The samples of erbium doped lithium niobate (Er:LiNbO₃) were prepared by standard Czochralski method and treated by Annealed Proton Exchange (APE) procedure to create planar wave-guide for further optical application. The position of Er atoms in the crystal lattice of pristine and APE treated Er:LiNbO₃ samples were studied by Rutherford Backscattering Spectrometry (RBS)-channeling method. The Er³⁺ ion position in the pristine and the APE treated Er:LiNbO₃ samples are compared.

PACS: 42.70.Mp, 61.72.Dd, 29.30.Ep, 82.35.Lr

1 Introduction

Characterization of progressive materials and structures non-destructive way is an important task in material engineering. Nuclear analytical methods using high energy ion beams from accelerators are very powerful tool for investigation of materials. In Nuclear Physics Institute of ASCR we provide standard nuclear analytical methods - Rutherford Backscattering Spectrometry (RBS), Elastic Recoil Detection Analysis (ERDA) which enable us to determine in fact all

¹Presented at SSSI-IV (Solid State Surfaces and Interfaces IV) Conference, Smolenice, Slovakia, 8–11 Nov. 2004.²E-mail address: mackova@ujf.cas.cz

elements with low detection limit of several ppm and good depth resolution - depth resolution of several nm should be achieved. Ion energy losses give us opportunity to evaluate the elemental depth profiles, it means to study also an interface composition and properties. RBS-channeling study is used for single-crystalline material study which provides information about the crystal quality and the host atoms position.

Polymer-metal interaction study

Wide range of applications of metallized polymers [1] in microelectronics has stimulated research of metal-polymer interaction. Polymers are the good candidates for fabrication of multilayer metallization structures on the chip level and for packaging. Mechanical and electrical properties of the metal-polymer interface is strongly affected by the degree of metal-polymer diffusion and intermixing [2]. Thus there is a basic need to understand the mechanism of metal diffusion in polymers and its effects on the structure and formation of metal-polymer interface.

Er:LiNbO₃ study

Optical amplifiers and lasers based on materials doped with rare earth atoms have large application potential. Lithium niobate (LiNbO₃), due to its very favourable electro-optical, acousto-optical and non-linear properties, is one of the most popular materials for these applications [3]. Annealed Proton Exchange (APE) was used to fabricate planar waveguides. Proton exchange (H⁺ for Li⁺) takes place in liquid proton source, typically an acid. This procedure increases the extraordinary refractive index, but it also causes changes of the crystal structure of the treated layers. To optimise the active function of the fabricated APE optical waveguides in Er:LiNbO₃ it is very important to know the exact positions of the Er³⁺ in the structures of both APE treated and non-treated Er:LiNbO₃.

2 Experimental

Polymer-metal interaction study

The samples were prepared by deposition of thin Ag layers on the polyethylenetereftalate (PET, C₁₀H₈O₄, $\rho = 1.397 \text{ g.cm}^{-3}$). Ag layers with typical thickness less than 10 nm were deposited using CVD or diode sputtering (BAL-TEC, SCD 050 system) techniques on polymer substrates. The deposition was performed at room temperature. In the case of diode sputtering (room temperature (RT), total argon pressure about 4 Pa, the electrode distance 50 mm and current 20 mA), deposition times were 50 and 80 s. The annealing was performed on air atmosphere in small annealing furnace up to 120°C. Metal concentration depth profiles we obtained from RBS spectra (2.2 MeV He⁺ ions, 170° laboratory scattering angle) using computer code GISA 3 [4]. ERDA measurement was performed with 2.7 MeV He⁺ ions and the protons recoiled under the angle of 30° were registered. X-ray Photoelectron Spectroscopy (XPS) was used to determine the fraction of embedded metal particles in near surface region of polymer. Measurements of photoelectron spectra were carried out on an angular-resolved X-ray induced photoelectron spectrometer ADES-400 (VG Scientific) using Mg K _{α} radiation (1253.6 eV) and a rotatable hemispherical energy analyser. The spectra were recorded at normal emission angle except those

recorded for quantitative analysis where both normal and 60° emission angles were used. The energy positions were referenced to the Cu 2p peak at 932.6 eV and Au 4f peak at 84.0 eV binding energy. Atomic concentrations were determined from XPS peak areas corrected for photoelectron cross-sections [5], the inelastic mean free paths [6], and experimentally determined transmission function of the energy analyzer.

Er:LiNbO₃ study

The congruent Er:LiNbO₃ single crystal containing 5000 ppm of Er was grown by the standard Czochralski method (Avtex Turnov). The crystal was cut into 0.7 mm thick wafers corresponding to x- ($\langle 11 - 20 \rangle$), y- ($\langle 01 - 10 \rangle$) and z - ($\langle 0001 \rangle$) cuts, in which the planar waveguides were fabricated by the APE process at 213°C for 3 hours using adipic acid as the proton source. The wave-guides were single mode at $l = 1.5 \mu\text{m}$ and the proton profile reaches about $10 \mu\text{m}$ deep into the wafer as does also the depletion of lithium. The RBS-channeling experiments were performed at the Forschungszentrum Rossendorf, Dresden, Germany using the beam of 1.7 MeV He⁺ ions from a Van de Graaff accelerator and standard measuring procedure [7]. The signals of the Er atoms and the host lattice LiNbO₃ in backscattered ions spectra are well separated due to scattering kinematics. From angular scan of backscattered ions through different axial channels the Er atom positions in the crystalline lattice were obtained for the pristine and the APE treated Er:LiNbO₃. The angular scans along the x $\langle 11 - 20 \rangle$, y $\langle 01 - 10 \rangle$, z $\langle 0001 \rangle$ axis were measured for pristine Er:LiNbO₃ samples and for the samples treated by APE technique.

3 Results

Polymer-metal interaction study

Annealing at higher temperatures may lead to degradation of the polymer substrate accompanied with emission of volatile, hydrogen or oxygen rich degradation products. This effect was thoroughly examined by RBS and ERDA techniques and no compositional changes were observed. Concentration depth profiles of diffusing metal atoms were determined from RBS spectra. On PET-Ag samples surface concentration decreases and deeper Ag penetration with increasing annealing temperature is observed. Diffusion coefficients for deposition times 50 s and 80 s were determined using standard procedure from the plot of $\ln(\text{concentration})$ vs. depth^2 [8]. Arrhenius plot for diffusion of Ag deposited by two deposition techniques and for different deposition times are shown in Figure 1.

Diffusion coefficients of Ag atoms deposited using diode sputtering are by one order of magnitude higher than those on the samples prepared using CVD technique. Diode sputtering enables one to prepare metal layers with low thickness facilitating high inward mobility of metal atoms. Higher diffusion coefficients are also observed for Ag layers deposited for 50 s in comparison with those deposited for 80 s (see Figure 1).

In the XPS spectra shown in Figure 2 the main part of C 1s peak C-C doesn't change its position; small uncertainty is connected with corrections on sample charging during XPS measurement. Most significant reduction of the C=O peak is observed for annealing temperature 70°C for both deposition times 50 s and 80 s. The data indicate that at the temperature 70°C a perturbation of C=O bond takes place. On the samples prepared by diode sputtering for 50 s, Ag

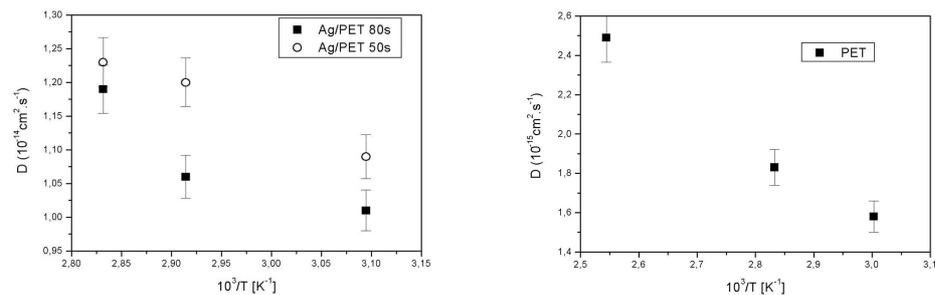


Fig. 1. Arrhenius plot of Ag deposited by diode sputtering at RT on PET substrate - deposition time 50 s and 80 s -left. Arrhenius plot of Ag deposited by CVD at RT on PET substrate -right.

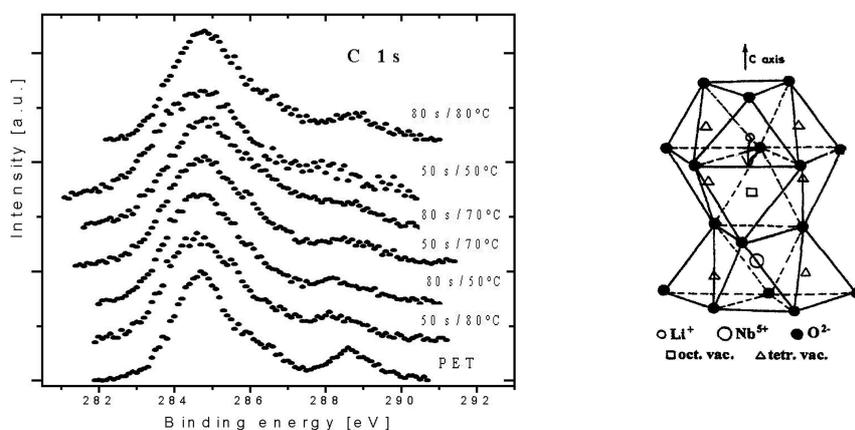


Fig. 2. XPS C 1s spectrum recorded from Ag deposited by diode sputtering for 50 s and 80 s at RT on PET substrate - left. The schematic picture of the basic volume cell of the free lattice sites in LiNbO_3 are marked by the squares (the octahedral site) and the triangles (the tetrahedral site)- right

fraction measured by XPS after removing a continuous Ag surface layer decreases significantly with annealing temperature see Table 1. It indicates the higher depth incorporation of Ag atoms as is referred in [9]. Low difference between Ag fraction XPS measured under the angles 0° and 60° indicates higher compactness of Ag layer deposited for 80 s, in comparison with the layer deposited for 50 s.

Tab. 1. XPS results - Ag fraction deduced from XPS after removing Ag bulk layer from polymer substrate

Sample deposition time / annealing temperature	Angle [°]	Ag [atomic %]
50 s/80°C	0/60	3.4/5.2
50 s/70°C	0/60	4.2/4.1
50 s/50°C	0/60	6.4/9.4
80 s/80°C	0/60	3/3.1
80 s/70°C	0/60	4.3/4.1
80 s/50°C	0/60	4.8/7
PET	0/60	0/0

Er:LiNbO₃ study

In the structure of LiNbO₃ crystal four different lattice sites are available which may be occupied by foreign ions: two substitutive octahedral sites (Li⁺ and Nb⁵⁺), an additional free octahedron and a tetrahedral vacancy site see Figure 2 on the right. The scan of yield of backscattered He⁺ ions along the < 0001 > axis of pristine Er:LiNbO₃ can be used to identify any position out of the z-axis, it means the tetrahedral site. The angular scan of the Nb host atoms through the < 0001 > axis is practically identical to that of Er atoms, so that it concluded that the Er atoms are located in three possible positions along the z-axis, i.e. the Nb⁵⁺, Li⁺ sites or the structural octahedral site. The scans through < 01 – 10 > and < 11 – 20 > axes were measured (see Fig. 3 above) to determine precisely the Er position inside the Li⁺ octahedron. If the Er atoms sit in the octahedral position a maximum in the scan through < 11 – 20 > axis should be seen [10], but this is not the case. From the measured angular scan shapes of pristine Er:LiNbO₃ samples and from the simulations published in [11] we can conclude that the Er³⁺ ions sit on the Li⁺ sites but they are shifted slightly in the direction along the z-axis. The shift along the z-axis direction of about 0.03 nm was found for the pristine Er:LiNbO₃ samples in accord with the data reported earlier for Yb³⁺ ions in Yb:LiNbO₃ [10]. The same analysis of angular scans we have done for APE treated samples - 3 cuts (Figure 3, the second row) and it indicates about 0.09 nm shift of the Er³⁺ ions in the z-axis direction. The shift of Er atoms after the APE treatment corresponds to the expansion of the Er:LiNbO₃ cell volumes. In the case of APE treated samples we observed the crystal lattice modification in RBS-channeling spectra which are indicated by an increase of RBS yield from the APE treated sample in comparison with that from pristine samples observed in aligned spectra.

4 Conclusion

Polymer-metal interaction study

The study on diffusion activity of Ag atoms in PET was done. The samples were prepared by CVD and diode-sputtering techniques on polymer substrate and the diffusion was initiated by annealing to temperatures near polymer glassy transition temperatures. The diffusion coefficients of the order of $10^{-14} - 10^{-15} \text{ cm}^2 \cdot \text{s}^{-1}$ were found in accord with the results reported earlier

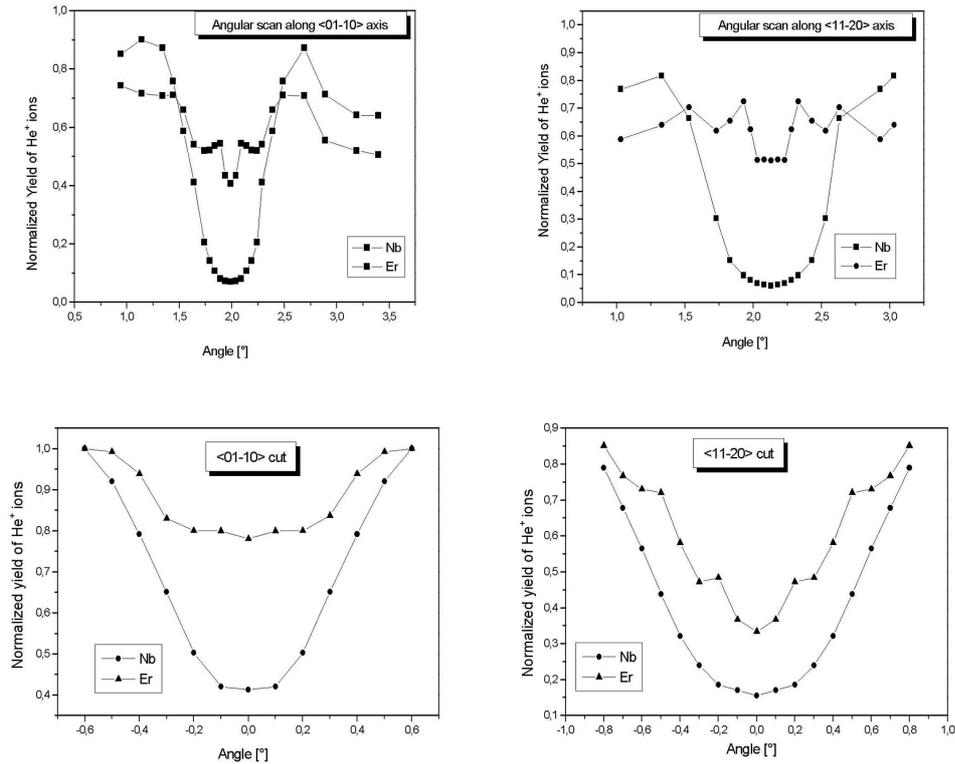


Fig. 3. The comparison of angular scans measured RBS-channeling method along axes $\langle 11-20 \rangle$, $\langle 01-10 \rangle$ of the pristine samples (the first row) of Er:LiNbO₃ and APE treated samples of Er:LiNbO₃ (the second row).

for other polymers [12]. Faster diffusion of Ag atoms was observed on the samples prepared by diode-sputtering technique and for lower deposition time. This may be due to the fact that CVD technique produces thicker and more compact Ag films.

Er:LiNbO₃ study

The RBS-channeling measurements show that the Er³⁺ ions in pristine Er:LiNbO₃ are located in the Li⁺ site but they are shifted by 0.03 nm in the z - direction. The shift from the Li⁺ site is connected with the larger size of the Er³⁺ ion, which is forced to move towards the bigger oxygen triangle. The shift of 0.09 nm observed in the APE treated samples can be explained by enlarged volume of the Er:LiNbO₃ elementary cell and also by the crystal modification created by the APE treatment.

Acknowledgement: This work was supported by Grant Agency of the Czech Republic under the project Num. 102/01/D069 and by MSMT under the project COST 527.100 and COST 527.90.

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