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INVESTIGATION OF PLASMA POLYMER AND NANO COMPOSITE POLYMER FILMS BY RUTHERFORD BACKSCATTERING SPECTROMETRY AND BY ELASTIC RECOIL DETECTION ANALYSIS ANALYTICAL METHODS[1]

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In this work, we have studied the composition of polymer thin films prepared by plasma polymerisation and d.c. magnetron sputtering. We investigated two sets of samples, one set Ag composite layers and the second set nitrogen containing plasma polymers, both deposited on the silicon substrate. The Rutherford Backscattering Spectrometry and Elastic Recoil Detection Analysis measurement was used to characterize the composition and to determine the element depth profiles in the deposited layers.

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1 Introduction

Several techniques can be applied for the composition study of thin polymer films, among them XPS (X-ray Photoelectron Spectroscopy) is most frequently used. The limitations essential to these methods leave some information unrevealed. XPS is very powerful method for determining the elemental composition, but it does not detect hydrogen and the analysis depth is only several nanometers. Thus, the application of such non-destructive techniques as Rutherford Backscattering Spectrometry (RBS) and Elastic Recoil Detection Analysis (ERDA) for the estimation of the element composition and depth profiling in plasma polymers is very favorable. In this study we focused on composite Ag/CH coatings and amine rich plasma polymer films. The Ag-CH coatings can be used in biomedical applications. Polymers containing silver are known for their antibacterial properties [1] and amine plasma polymers are applied for the development of acoustic wave sensors [2], microfiltration membranes [3] or enzyme electrodes. It is usually important to know, how the external parameters influence the composition of plasma polymers.

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2 Experimental

Two sets of the samples were investigated. The first one - plasma polymerized diaminocyclohexane layers (DACH) and the second one - Ag:C:H composite layers on the silicon substrate. Amine containing plasma polymers were deposited by Plasma Enhanced Chemical Vapour Deposition (PECVD) of diaminocyclohexane (DACH, 5 Pa, 0.85 cm^3/min) in a tubular reactor with capacitively coupled ring electrodes (13.56 MHz). The experiments were performed in continuous wave (CW) and pulse mode (duty cycle 0.1). The average power was varied between 2 and 30 W. Composite Ag/CH films were prepared by DC magnetron sputtering of silver target in a mixture of Ar and n-hexane. The flow rate of the gases was varied independently to achieve different Ar/n-hexane ratios, but the total flow rate (7.7 cm^3/min) and the pressure of gas mixture (2 Pa) were held constant. The deposition was performed at 0.1 A current; the deposition time was 5 min for each sample. The variation of Ar/n-hexane ratio allows to control the film composition: the lower values result in low concentration of Ag in C:H matrix, while the higher ones lead to nearly metallic silver coatings.

The RBS and ERDA analyses of prepared samples were performed in vacuum target chamber using the 2.745 MeV alpha particle beam and 2.4 MeV proton beam. The ion beam was provided by electrostatic accelerator. The RBS and ERDA techniques, based on elastic scattering of charged particles, enabled us to determine the content and depth profiles of C, H, N and Ag elements with the sensitivity from 10^{11} - 10^{15} atoms/cm ^{2}. The RBS spectra were evaluated by GISA 3 code [4]. The RBS spectra of the back-scattered protons 2.4 MeV are useful for the determination of the light elements C, O, N in the deposited layers due to the resonant backscattering cross section, on the other hand the depth resolution is lower in this case (see, please, RBS spectra of backscattered protons under the scattering angle 170^o in Figure 1a). The RBS measurement with 2.745 MeV alpha particles gives us more accurate information about Ag depth profile in the deposited layers. We can distinguish non-homogeneous distribution of Ag within the deposited layer due to the better depth resolution in the backscattered alpha particle spectra. Also we obtain the information about the thickness of the deposited layers. The accuracy of RBS amount determination is in the range of 2 atomic $\%$.

In ERDA measurement we detect the recoiled hydrogen ions from the sample using the glancing geometry arrangement (scattering angle 30 ^{o})- see ERDA spectra in Figure 1b. The depth profiles could be determined non-destructively to the depth of 5μm with a typical depth resolution of 40 nm. ERDA spectra were evaluated by SIMNRA5.0 [5]. The accuracy of the hydrogen determination is in case of the samples deposited on silicon substrates in the range of 2 atomic $\%$.

3 Results

Two sets of the samples were measured and the composition was obtained from RBS and ERDA spectra evaluation. The composition is evaluated in atomic $\%$ and the thickness of the layer in atoms/cm^2.

The deposition of amine containing plasma polymers was performed in a flow of DACH monomer. The dynamic equilibrium establishes fast after the ignition of the discharge, provided that all external parameters of the discharge are held constant. This means that the concentration of various species is constant and various processes run with the constant rates. The film grows

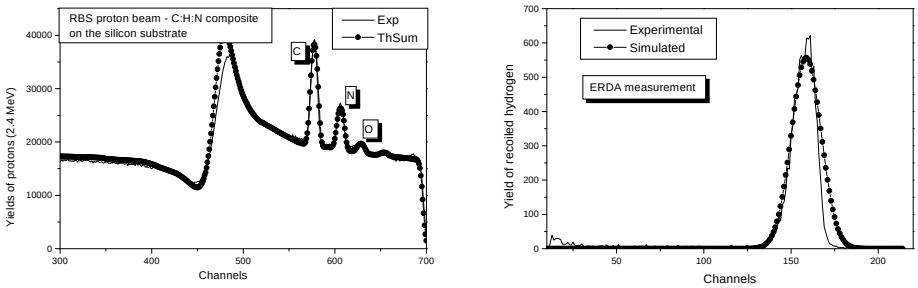

Fig. 1. a) The RBS (2.4 MeV protons) spectrum of amine polymer layers on silicon (C 39%, N 8%, H 50%, O 3% thickness 7800 E15 atoms/cm^2) , b) ERDA measurement of the Ag:CH layer deposited on the silicon using alpha particles 2.745MeV.)

uniformly and the element profiles are constant (Fig. 2a, b). The samples prepared in CW mode at 2 and 5 W power have the same composition (Fig. 2b). The C/N ratio is 4.56 for the samples 6R, 5R. The pulse mode yields the films with a little lower hydrogen content (Fig. 2a). The C/N ratio is 4.0 and 4.89 for 1M (2 W) and 6M (30 W) samples, respectively. The surface layers of amine plasma polymers have the lower nitrogen concentration, caused during aging, on the one hand, by hydrolysis of amines by atmospheric H_2O with elimination of NH_3 or by surface restructuring, on the other hand. The pulse DACH layers seem to be more susceptible to these changes than CW ones.

The depth profiles of different elements in Ag/CH composite films are shown in the Fig. 3 a, b. The Ag profile is not homogeneous, the Ag surface concentration is lower than concentration deeper within the deposited layer. We ascribe it to the known 'target poisoning' effect [6]. At the beginning of the deposition the positive ions collide with the pure silver target, efficiently sputtering Ag atoms, and the first deposited layers have the high Ag content (40-50%). The various species of n-hexane molecules produced by the discharge take part in the formation of hydrocarbon polymer on adjacent surfaces as well as on the silver target. The lower n-hexane concentration in the gas mixture (Fig. 3a) gives the lower polymerization rate and the resulted films contain more silver (48% for Ar/n-hexane 7/0.7 cm^3/min sample 22.5 and 43% for Ar/n-hexane 6.4/0.9 cm^3/min sample 23.5). As the process is going on, the target gets covered by non-conductive CH coating. The efficiency of Ag sputtering decreases and the Ag concentration in the films falls down, while the concentration of C and H increases. In our case, the Ag content in the surface layers is two times lower than within the film. This Ag concentration variation should be removed by the accuracy in choosing the deposition time and other parameters of the process and has been avoided in newer samples by means of optical emission spectroscopy.

4 Conclusion

The main goal of the RBS and ERDA measurement was to characterize the composition and to determine the depth profiles of the elements in the deposited layers. RBS/ERDA techniques are shown to be useful in understanding and optimizing the dynamics of plasma deposited thin film growth.

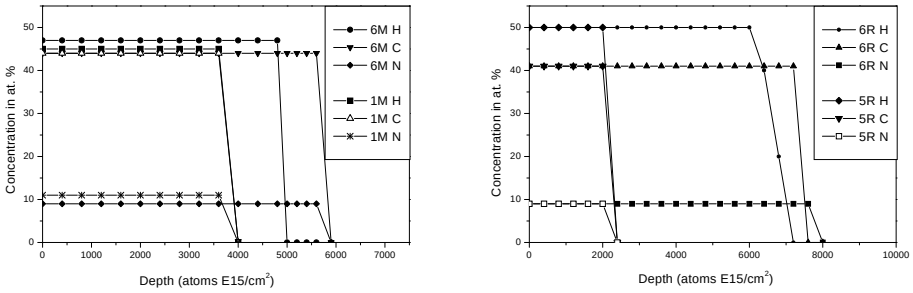

Fig. 2. The concentration depth profile of C, H, N elements in amine plasma polymer layers. Samples a) 6M (30W), 1M (2W) and b) 5R (2W), 6R (5W).

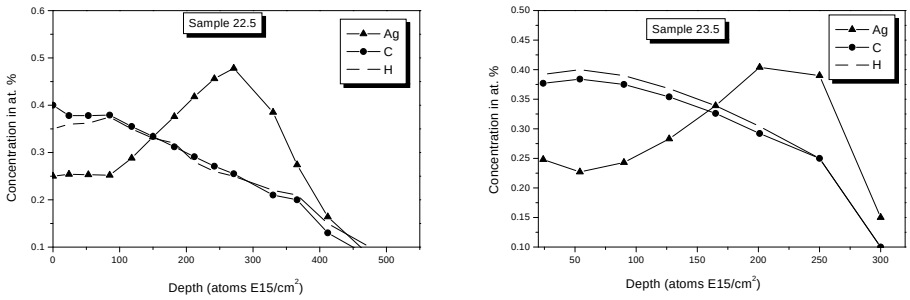

Fig. 3. The concentration depth profile of Ag, C, H elements in Ag/CH composite films. Samples a) Ar/n-hexane 7/0.7 cm^3/min sample 22.5 b) Ar/n-hexane 6.4/0.9 cm^3/min sample 23.5

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