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The characterization of PEEK, PET and PI implanted with Co ions to high fluences

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ABSTRACT

Polyimide (PI), polyetheretherketone (PEEK), and polyethylene terephthalate (PET) foils have been implanted with 40 keV Co^+ ions at room temperature to the fluences ranging from 0.2×10^{16} cm^{-2} to 1.0×10^{17} cm^{-2}. Co depth profiles determined by RBS have been compared to SRIM 2008 calculations. The measured projected ranges R_P differ slightly from the SRIM simulation because of the compositional changes in polymers implanted to high fluences; especially the widths of the Co profiles are much larger than those simulated by SRIM. Oxygen and hydrogen depletion has been examined using the RBS and ERDA techniques. The surface morphology of the implanted polymers has been characterized using AFM. The PET polymer exhibits lower oxygen escape than the PI and PEEK, but the surface roughness at PET has been affected most significantly after the implantation. Implanted Co atoms tend to aggregate into nanoparticles, the size and distribution of which has been determined from TEM micrographs and using image analysis. The largest diameter of Co particles has been found in implanted PET.

1. Introduction

Systems combining dielectrics with metal nanoparticles are of interest for their potential optical applications, in magnetooptic data storages, nonlinear optical switches and directional connectors [1]. The nonlinear optical properties of metal–polymer composites are connected with the local enhancement of the local electromagnetic field at metal nanoparticles, leading to a high nonlinear susceptibility of the third order [2]. Ion implantation changes polymer properties because of radiation degradation and the introduction of implanted atoms. At higher fluences, the implanted atoms may aggregate and metal nanoparticles are formed. These processes may be well controlled by an appropriate choice of metal ions, their energy, current and fluence. This makes it possible to examine the electrical properties of the composite, such as the insulator-to-metal transition and the evolution of the mechanisms of the electrical-charge transport from a variable range hopping through the carbon-rich phase of the polymer and metal inclusions up to a pure-electron conductance via percolating metal nanoparticles [3]. The main motivation for this experiment was the preparation of nanoparticles in different polymers and the characterization of their morphology in connection to the polymer matrix structural changes and their electrical properties.

2. Experimental

The 50-μm thick foils of polyimide (PI), polyetheretherketone (PEEK), and polyethylene terephthalate (PET), supplied by Goodfellow, Ltd., were implanted with 40 keV Co^+ ions to the fluences ranging from 0.2×10^{16} cm^{-2} to 1.0×10^{17} cm^{-2} at the ion beam accelerator ILU-3 of the Kazan Physical-Technical Institute, Russia. The implantation was performed at RT and at an ion current density of 4.0 μA cm^{-2}. The depth profiles of the implanted Co atoms and the composition of the implanted layers were determined by Rutherford back-scattering spectrometry (RBS) and elastic recoil detection analysis (ERDA). RBS spectra were measured using a beam of 2.0 MeV He^+ ions. An Ultra-Ortec PIPS detector recorded He^+ ions scattered at a 170° laboratory scattering angle. ERDA spectra were measured using 2.5 MeV He^+ ions. The primary beam comes at an angle of 75° with respect to the sample surface normal, and hydrogen atoms recoiled at a scattering angle of 30° were registered with a detector covered by a 12-μm Mylar foil. The typical

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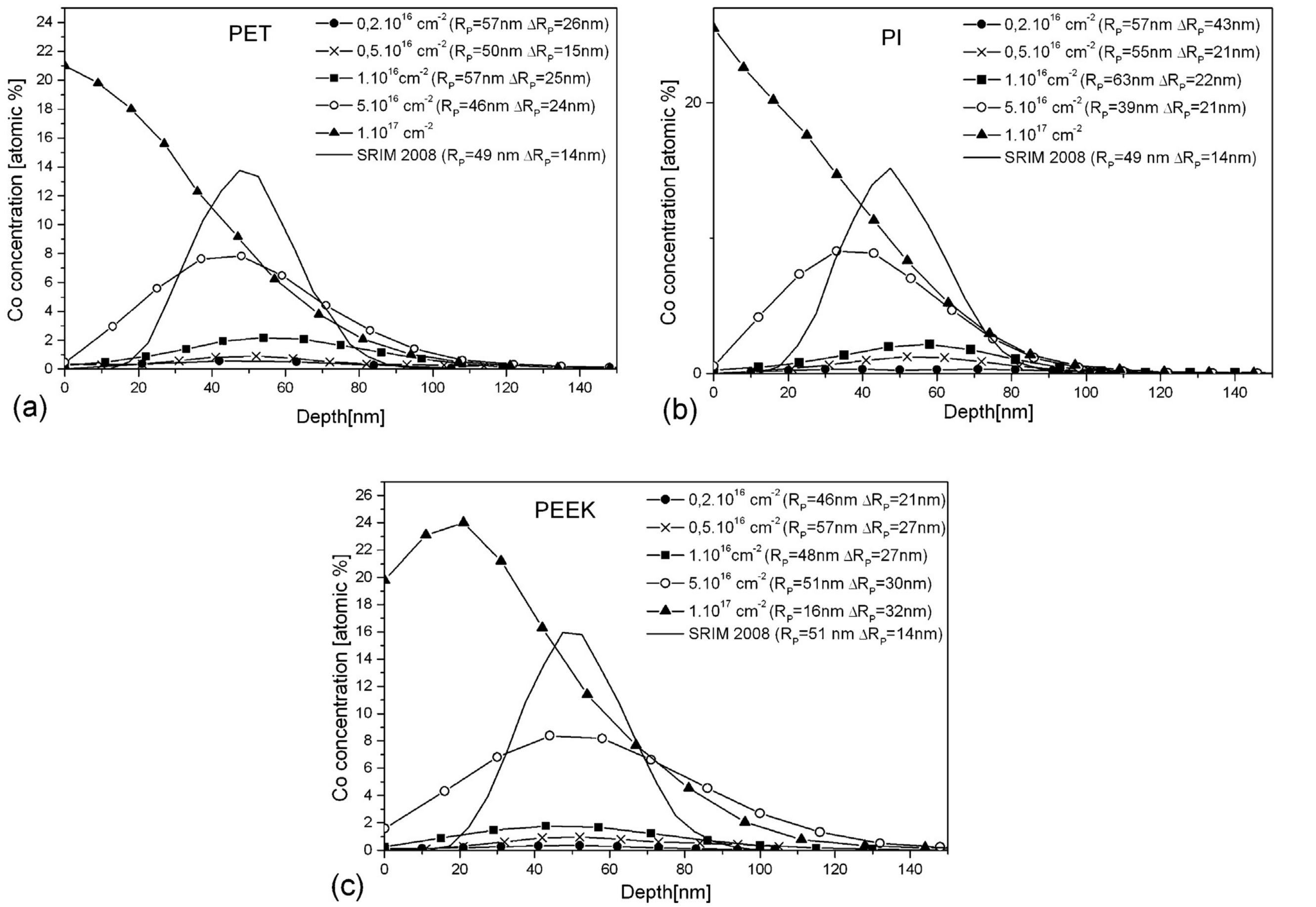

Fig. 1. The Co concentration profiles determined by RBS for the implantation fluences ranging from 0.2×10^{16} cm^{-2} to 1.0×10^{17} cm^{-2} with experimental and simulated R_P and ΔR_P in (a) PET, (b) PI and (c) PEEK.

intensity of the incoming beam was 20 nA. To reduce the effects of sample degradation during the RBS/ERDA analysis, several particular spectra were measured on different beam spots and the final spectrum was obtained by summing the individual spectra. The RBS and ERDA spectra were evaluated using the GISA 3.99 [4] and SIMNRA 6.06 [5] codes, respectively, utilizing cross-section data from IBANDL [6]. RBS and ERDA methods are suitable for the implant specie depth profiling, but in the case of shallow implantation profiles we have to include the surface roughness parameters to avoid the deteriorating of depth profile via the surface roughness.

The surface morphology and roughness were examined by atomic force microscopy (AFM) using Digital Instruments CP II Veeco, with silicon-doped probes RTESPA-CP and a spring constant of 20–80 N/m. AFM parameters were included in depth profiling analysis of RBS spectrum evaluation. All AFM measurements were carried out in the tapping mode in the ambient atmosphere and at room temperature. The mean roughness value (R_a) was calculated as the arithmetic average of the deviations from the centre plane of the sample [7]. Transmission electron microscopy (TEM) was performed on a TEM microscope JEM 200 CX at an accelerating voltage of 100 kV. Ultrathin cross-sections (about 60 nm) were cut from the centre of the polymer foils, fixed in epoxy resin (Durcupan), transferred to TEM microscopy grids and sputtered with a thin carbon layer.

3. Results and discussion

The depth profiles of the Co atoms implanted to the fluences ranging from 0.2×10^{16} cm^{-2} to 1.0×10^{17} cm^{-2} into PET, PI and PEEK are presented in Fig. 1a–c, respectively. The measured profiles are compared with those predicted by the SRIM 2008 code [8]. It is evident that the measured profiles are shifted towards the specimen surface and the profile widths are broader as compared to those calculated especially in the case of the highest implantation fluence, namely 1.0×10^{17} cm^{-2}.

The measured projected ranges R_P (in the case of the highest implantation fluence, 1.0×10^{17} cm^{-2}, cannot be extracted in PET and PI) and the range straggling ΔR_P extracted from Co depth profiles in PET, PI and PEEK is presented in Fig. 1a–c and compared with the corresponding SRIM ones. For all polymers, R_P was found to be in reasonable agreement with prediction within the frame of RBS uncertainties up to an implantation fluence of 0.5×10^{16} cm^{-2}. Above this implantation fluence, R_P became 25% lower than those predicted. Range straggling ΔR_P can also exceed the SRIM calculated ones by a factor of two. The discrepancy between the measured and predicted profile parameters at high implantation fluences is caused by the fact that the SRIM simulation does not take into account the compositional and structural changes of the polymer substrate in the course of the implantation. Depletion of volatile components and fragments, dynamic changes in the density of the implanted layer etc. may play a crucial role (see e.g. [9]). During the implantation, the polymer undergoes gradual compositional and structural changes and the resulting depth profile is in fact a sum of the depth distributions accumulated during various stages of the implantation process [12]. In the present case, the observed discrepancies are not so dramatic as in our previous experiment with 40 keV Ni^+ ion implantation [9], which is connected to the lower Co implantation fluences used in this case.