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SIMS Investigations of Ion Beam Induced PVK Fragmentation

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Summary

The mass spectra of secondary ions emitted from PVK thin layers under 2 keV Xe^+ bombardment were measured. The charasteristic elemental and molecular ions emitted were specified. The temperature dependence of the secondary emission was also measured. The results obtained were briefly discussed in terms of the ion beam-induced polymer structure fragmentation.

Introduction

The thermal stability of the poly-N-vinylcarbazole (PVK), involving fragmentation process of it s structure in vacuo was investigated by means of DTA, TG and pyrolysis methods (PIELICHOWSKI 1972, CHU et al. 1975, PIELICHOWSKI et al. 1980). The N-vinylcarbazole monomer mass spectrum obtained by an electronic impact was also reported (BARRALES-RIENDA et al. 1975). On the other hand the ion implantation into semiconductors and metals was succesfully applied in the field of materials modyfication. Implantation technique seems to be promissing also for polymers (SIGMUND 1984). The first reports on the ion beam-polymer surface interaction were connected with investigations of polymeric negative and positive resists used in integrated circuits technology (OKUYAMA et al. 1978 HALL et al. 1982). Recently ion implantation technique was used as a method of dopping of atomic acceptors such as As, Cl, Br, I into polymeric matrix (PVK, polyacethylene, poly-p-phenylene sulfide and others) – (JEDLINSKA-OBRZUT et al. 1983, BANKS et al. 1982, MAZUREK et al. 1983). It was proved very sufficient in polymer conductivity increase up to the metalic level.

In all above mentioned investigations the main attention was paid on the changes of the polymer properties induced by an ion bombardment. On the other hand ion implantation involves many different primary and secondary processes. The energy of primary ions is distributed in the bulk, the bonds between target atoms are broken and the atomic mixing inside the implanted sample occurs. As a result the gas evolution, free redical formation and secondary chemical reactions take place. These processes lead to several kinds of secondary emissions outside the sample such as neutral particycle emission (sputtering), secondary ion and electron

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emission and photon emission. The secondary ion emission can be monitored by means of SIMS technique and can carry the information on the polymer structure fragmentation occuring under ion beam influence. The lack of information published on this emission from polymeric surface was motivation of our investigations presented in this paper. In our previous work (BARBASZEWSKI et al. 1984), we studied the deposition of inert gas ions in PVK by means of SIMS. The dependence of secondary preimplanted ion emission on the sample temperature, the energy of primaries and the sample over-molecular structure was observed. In the presented work we aimed at the secondary atomic and molecular ion emission with their temperature dependence in low damaging conditions in vacuo. As far as we now this is a first publication of the secondary emission mass spectrum of the PVK thin layer.

Experimental

The ion source, magnetic separator, acceleration unit and the sample chamber were described previously (BARBASZEWSKI et al. 1978). The secondary ions were analysed by the 200 mm long quadrupole mass spectrometer with off-axis electron multiplier. The SIMS measurements were performed in low damaging conditions using xenon ions with energies equal 2,3 and 4 keV as the primaries. The Xe^+ ions were chosen taking into condideration the minimum effect of trapping of inert gas inside the PVK structure, which was found in our previous work (BARBASZEWSKI et al. 1984). The total pressure of residual gasses during measurements in the sample chamber was about 10^{-10} Torr.

The N-vinylcarbazole (Fluka AG), (5g) was polymerized at 70°C in benzene (50 ml) solution for 8 hrs in the presence fo AIBN (0.01 g) initiator. Polymer was precipitated by adding methanol and after washing three times with methanol it was dissolved in benzene. The benzene solution was treated with methanol and after precipitation and washing with methanol the polymer was dried at 60°C in vacuum. The yield of polymer was about 83%. The molecular weight was 30000 ± 1500. The PVK layers were prepared from the clean polymer by casting from solution on a stainless steel substrates (3 cm^2).

The cleaning and preparation procedure were identical as previously. The positive and negative secondary ions were analysed. The sample temperature was adjusted and stabilized, and the temperature dependence of the SIMS spectra was observed in the range from 295 up to 480 K.

Results and discussion

In the Fig.1 the mass spectrum of secondary ions emitted from PVK polymer is shown. The energy of primary Xe^+ ions was equal 2 keV and the sample temperature was 295 K. The SIMS spectrum is presented by the full lines. In the same figure the N-vinylcarbazole (monomer) mass spectrum obtained by an electronic impact with electron energy 70 eV after Barrales-Rienda is demonstrated (doted lines) in order to compare both fragmentation processes.

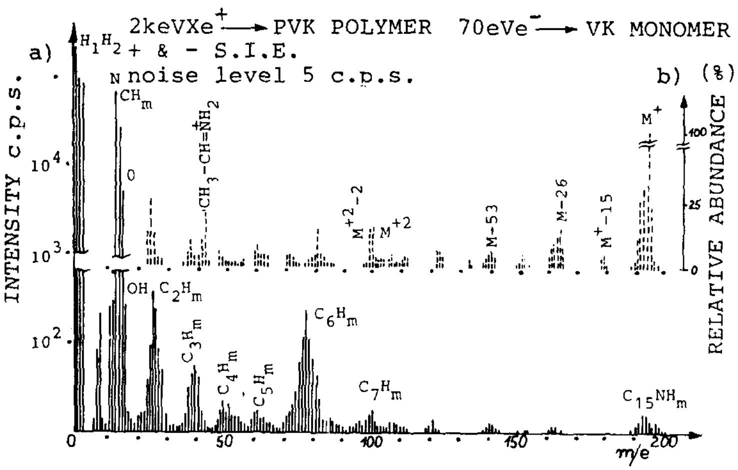

Fig.1. The mass spectrum of secondary ions emitted from the PVK sample
a) under Xe$^+$, 2 keV ion bombardment (full lines)
b) under 70 eV electron beam (doted lines)

Becausе of difficulties in quantitative analysis of the SIMS data, the main attention was paied on the comparison of m/e positions of characteristic groups in both spectra. Electron beam induced mass spectrum was originally normalised in intensities. The ion beam induced mass spectrum was shown in arbitrary unit because of the lack standards for emission from polymers. Electron beam induced fragmentation of monomer practically does not involve a gas evolution. It is due to other origin of the process, but mass positions of other characteristic groups show the similar sequences. The main differences are observed in the m/e ranges 70–85 and about 190.

Under electron bombardment very intensive monomer ions (M$^+$) emission was observed – m/e = 190. During Xe$^+$ ion bombardment only very weak ionised monomer groups emission is observed. In this case the monomeric units could be emitted as neutrals.

We paid the main attention on the fact of intensive emission of the C_6H_m – type ions in the m/e range 70–85. It implies a strong fragmentation of monomeric units of polymer, induced by ion beam. It was stated that under Xe$^+$ 2 keV ion bombardment (Fig.1; full lines) the following processes occurs; gas evolution and emission (H$^+$, H_2^+ , N$^+$, O$^+$, OH$^-$); emission of complex ions of C_nH_m – type with n up to n = 8 value; the integral emission intensity maximum take place for n = 6, i.e. for "benzenic" types of secondary ions. The intensity of C_nH emission depends nearly monotonically on n value. It is shown in the Fig.2 where $I = \sum_{m} C_nH_m$ for n = 1–10.

The exeptionally strong emission for n = 6 confirms the fragmentation of carbazolic side groups by breaking of the N–C bonds between polymeric chain and side groups connected with opening of the carbazole ring and N$^+$ ions emission. The energy of primary ions deposited

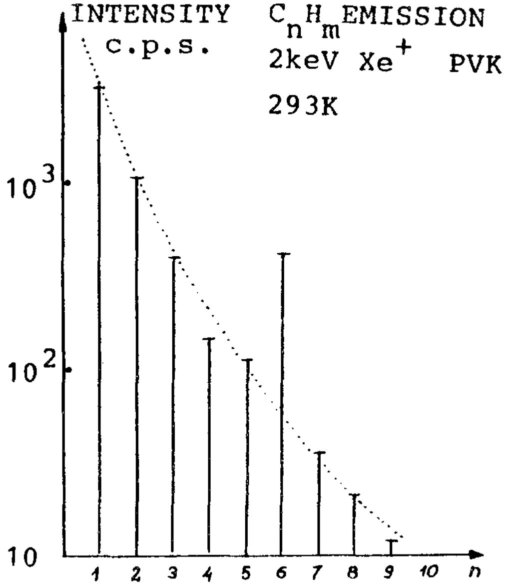

Fig.2. The intensity of C_nH_m ions emission under 2 keV Xe^+ bombardment at the 293 K.

into a sample can be effectively transfered along the polymeric chain because of the macromolecules stiffnes (rod-like type). Thus, the degradation process similar to that described in the literature and called "unzipping mechanism" can take place. Additionally excitation energy transfer causes immediate fragmentation of monomeric groups. As a result intensive emission of complex ions with n =1–5 occurs. They originates from side groups (mainly) and aliphatic chain.

The thermal dependence of the secondary mass spectra was measured with the temperature step of 10 K. Results are shown in the Fig.3. In a range up to about 0.5 T_g; (T_g – glass point temperature of PVK – 212°C) the secondary emission is almostindependent on the sample temperature for all hydrocarbon ions. Above 0.6 T_g emission intensity increases, especially for the low n-values. This process was observed to be reversible with temperature cycling involving heating and cooling of the sample up to the 0.9 T_g value.

The emission of oxygen ions originates probably from the residual solvent and air admixtures, which cannot be totally removed during cleaning. It is also due to the relatively high probability of oxygen ionization. The temperature independence of N^+ emission, confirms the side groups fragmentation as a straight process occuring on or at the sample surface. The lighter fragments emission increase with temperature (above 0.5 T_g) can involve an additional thermally activated process taking place under the sample surface, but the thermal energy in the temperature range used is too low and the mechanism of lihter fragments emission must involve much higher local temperature values. Thus, the thermal spike mechanism (SZYMONSKI 1984) should be taken into consideration. The obtained results should be treated as a first approximation of the investigated phenomenon.

Final remarks

During the modification of the polymeric thin layer by means of ion implantation technique, the fragmentation and secondary emission processes should be also taken into consideration. The all types of above mentioned straight and secondary processes will be a subject of more detailed investigation. The further investigations should enable us to prove in what extend the terms of collision cascade (SIGMUND 1969, BARBASZEWSKI 1983) and thermal spike (SZYMONSKI 1984) succesfully introduced in the metal and semiconductor fields, can be useful in case of polymers of rod like type macromolecules.

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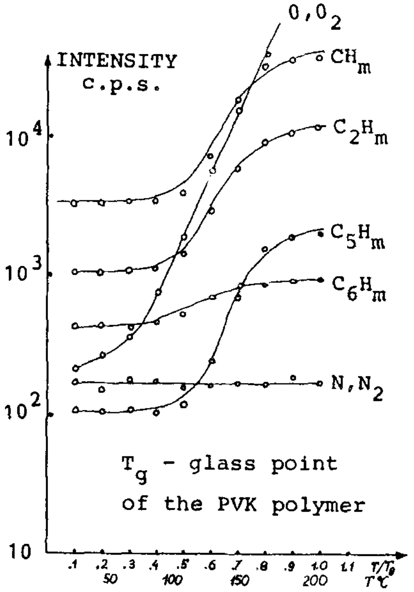

Fig.3. The temperature dependence of the secondary ion emission from the PVK sample.

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