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MOLECULAR STRUCTURE OF IONS IN FLUORINE CONTAIN DIELECTRICS AT THE SECONDARY ION MASS-SPECTROMETRY (SIMS)

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Abstract- In the present paper is given the results of investigation of secondary ions formation mechanisms from a surface of polymeric dielectrics. By calculation of secondary ions' relative yield in dielectric mass spectrum and the results comparison with various mechanisms, an attempt was made to explain the mechanisms of ion formation at the process of bombardment of dielectric surface by accelerated particles.

Keywords: Time of Flight Mass-Spectrometry**,** Secondary Ion Mass-Spectrometry, Polymer, Fluorine Contain Dielectrics.

I. INTRODUCTION

The Secondary Ion Mass-Spectrometry (SIMS) being widely used for the analysis of metal and semiconductor materials, since recently started to be applied to the investigation of the polymeric dielectrics. The experimental materials collected by now allow generating some regularity of the secondary ion emission from the molecular substances and to reveal the mechanism of secondary ions formation.

On the other hand, this method, as similarly as other mass-spectrometric methods of the element analysis, is associated with a main problem: obtaining of reliable quantitative data. Carried out investigations and experiments [1, 2] showed that the composition of secondary ions mass spectrum not always matches to a true element composition of the sample. The reasons of this mismatch are an unequal yield of the secondary ions of various elements caused by the peculiarity of atomization and ionisations; and sometimes also by discrimination on mass in the systems of partitioning and registration of ions.

For registration of this mismatch in [3, 4] it is offered to use the relative sensitivity coefficients (RSC) of defined elements in relation to the interior standard which allows to reduce systematic errors on the average approximately up to 20%. However, a process of the manufacturing of standard samples with the consideration of rigid conditions for Secondary Ion Mass-spectrometry is extremely inconvenient; therefore, determination of the relative yields of secondary ions by means of theoretical or empirical expressions still remains a problem. In the present work there was made an attempt to evaluate the relative yields of secondary ions from a surface of some dielectrics on basis of experimental data and in terms of it to explain the mechanisms of secondary ions formation.

II. CONDITION OF THE EXPERIMENT

The experiments were carried out on a facility, schematically presented on a Figure 1. Accelerated Argon's atoms beam has been gained by the way of recharging of argon ions in the ionisation chamber (1) by electron impact method. Accelerated Ar^+ in ionisation chamber transiting through the recharging chamber (2) recombine by means of electrons, emitted from the thermal cathode. The braking field (6) being erected on the argon atoms paths promotes to cut argon charged particles. So, at the length of recharging chamber of 100 mm and pressure 10^{-2} Pa it was managed to recombine more than 10% of Argon ions quitting the ionic gun. It allowed to gain a beam of atoms of an argon with the energy of 2.0-2.5 kilo electron volt (keV) and density 10^{10} a/(cm^2·s).

Warmed up substrate (4) with the explored samples with thickness 0.1 - 0,6 mm, moved in vacuum chamber by means of the vacuum lock (8) [5]. The vacuum of 10^{-4} Pa in the chamber was maintained by fore-vacuum and high-vacuum pumps. The secondary ions, emitted from a surface of the sample, were drawn out from an interaction area of neutral particles of a surface by means of extracting electrodes (5) on which an impulse voltage of 1500 V was applied, concerning a substrate, and with duration 10^{-6} sec. This promoted to a direction and focusing of secondary ions, simultaneously decelerated secondary electrons. The secondary ions packet was guided onto the inlet of axial-symmetric analyzer [6]. Transiting through the entrance diaphragm (7), the drift space (6) and then output diaphragm (10), molecular ions were separated on M/z in the analyzer of ions, creating a mass spectrum yield. The main demand to the ionic gun was the major quantity of an ion current. As mass-spectrum of the secondary ions depends on energy of bombarding particles not much, it is quite acceptable their straggling on energies within the ranges of 10-20%.

The special attention was given to the purity of a target at its preparation for further investigation. The presences even several monolayer of alien molecules on a surface, garbles the secondary-emission mass spectrum of investigated material essentially. Refining of a dielectric target's surface from organic matters appears more simple than metallic others [7, 8]. Therefore, in the vacuum condition of 10^{-4} Pa the heating of a target up to the temperature of 150-200 °C within one hour leads to its full cleaning of the adsorbed molecules. Surface clean control performed by a mass spectrum of the secondary ions. The target was considered as cleared if the intensity of peaks caused by hydrocarbon pollution did not exceed some percents from intensity of main peaks in a polymeric compound mass spectrum.

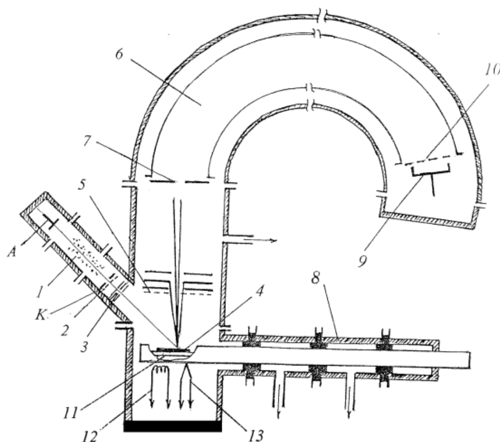


Figure 1. Experimental facility

III. RESULTS AND DISCUSSIONS

The correlation between a structure of a molecule and distribution of intensities in the secondary-emission mass-spectrum allows using a method of Secondary Ion Mass-spectrometry (SIMS) for investigation of the structure of polyatomic molecules, in particular of polymeric compounds. There were investigated polymeric compounds of poly tetrafluoroethylene $(CF_2\text{-}CF_2)_n$ and polytrifluorochloroethylene $(CF_2\text{-}CFCl)_n$ and copolymers of tetrafluoroethylene with ethylene and trifluorochloroethylene with vinyliden chloride. The targets have been prepared by press-fitting on metallic substrate in a form of film with the thickness 0.1-0.3 mm.

Typical mass spectra of the secondary ions, investigated polymeric compounds, gained at bombing the targets by an accelerated atoms beam of argon with the energy of 2.5 kilo electron-volt (keV) are given on Figure 2. Apparently, from a Figure 2, both polymeric compounds have rich enough combination of the secondary ions reflecting an element composition of the substance. The view of a mass spectrum is spotted as also by the structure of molecules. Good instances in this respect are masses - spectra of vinyliden chloride and tetrafluoroethylene with ethylene. These polymeric compounds have an equal element composition and differ only by the structure of molecules [7].

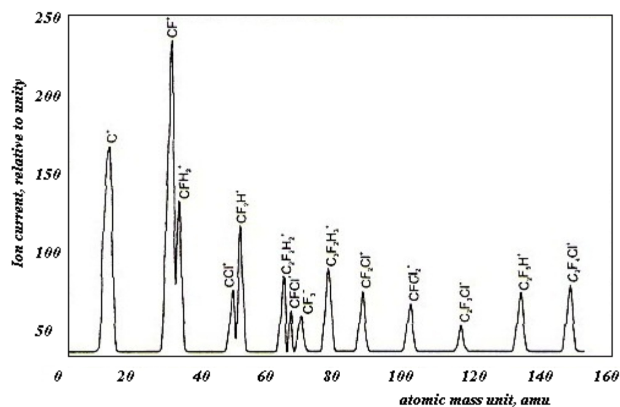


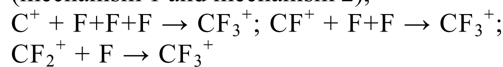
Figure 2. Mass-spectrum of polytetrafluoroethylene $(CF_2\text{-}CF_2)_n$

If to compare mass-spectra of copolymers with mass-spectrum of appropriate polymeric compounds as it is mentioned in [7], the firsts represent some superposition of mass-spectra of appropriate polymeric compounds. Indeed, it is observed intensive enough peaks matching to the ions of CCl^+, $CFCl^+$, $CFCl_2^+$, $C_2F_3Cl^+$, $C_3F_4Cl^+$ which in its turn is the most typical in mass- spectrum of polytrifluorochloroethylene (Figure 3), and the peaks matching to ions CFH^+, CFH_2^+, CF_2H^+, $C_2F_2H_2^+$, $C_3F_2H_3^+$ are the most typical and can be used for estimation of a composition of a polymeric compound.

Let's consider the correlation between the relative yield of secondary ions and molecule structure on an example of ions CF_3^+ and CF_2H^+ in mass-spectrum of polytetrafluoroethylene and also CF_3^+ and $C_2F_2Cl^+$ in mass-spectrum of trifluorochloroethylene with vinyliden chloride.

In [7] it is offered 4 possible mechanisms of formation of secondary ions as a result of ion-molecule reaction which are growing out of interacting of separate atoms, being formed at the bombarding atoms of argon with a surface. As a result of regrouped processes when atoms of other molecules are associated to the fission ion during sputtering of the material at the target. To define, which of these mechanisms is actually responsible in formation of secondary ions, the calculation of the relative ionic yields was carried for each of CF_3^+ and CF_2H^+ from copolymers and ions CF_3^+ and CF_2Cl^+ from polymeric compounds. Calculations were made in assumption that formation of the charged fragments CF^+ or CF_2^+ happen with equal probability.

According to the offered mechanisms, ion CF_3^+ can be formed at the expense of ion-molecule reaction (mechanism 1 and mechanism 2),



$C^+ + F{+}F{+}F \rightarrow CF_3^+$; $CF^+ + F{+}F \rightarrow CF_3^+$;

$CF_2^+ + F \rightarrow CF_3^+$

or regrouped processes (mechanism 3) when F of other neighbouring molecule CF_2^+ joins to the fission-product ion of CF_2^+. At last, the fourth mechanism considers the possibility of pickup atoms of fluorine of molecules CF_2 by ion CF_2^+ which meet each other in the transit to its yield from a warmed-over section of a surface.

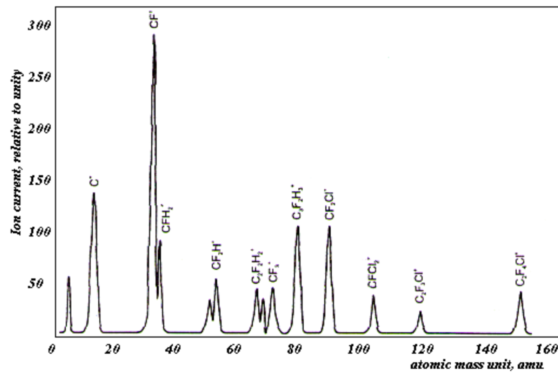


Figure 3. Mass-spectrum of polytrifluorochloroethylene $(CF_2\text{-}CFCl)_n$

Formation probability of ions CF_3^+ and CF_2H^+ have been calculated as follows. For creation of CF_3^+ ion it is necessary, first of all, CF^+ (or CF_2^+) to be created at the impact of bombarding atom, the probability (P_{CF}) of which is proportionally to the concentration (N_F) of fluorine atoms in a copolymer. Secondly, it is necessary joining two atoms of the fluorine to CF^+, the probability of this is proportional to N_F^2. Thus

$$P_{CF3} = P_{CF3} \cdot P_{CF2} = \alpha\, N_F \cdot \beta\, N_F^2 \tag{1}$$

where α and β are the proportionality coefficients.

The formation of CF_2H^+ ions can be performed by attaching atoms H and F to the fission-product of ion CF^+ or/and by attaching two atoms of fluorine to ion CH^+. Both these processes are progressing with an equal efficiency. Then

$$\begin{aligned} P_{CF3} &= P_{CF} \cdot P_{FH} + P_{CH} \cdot P_{2F} = \\ &= \alpha\, N_F \cdot 2\beta\, N_F \cdot N_H + \alpha\, N_H \cdot 2\beta\, N_F^{\,2} \end{aligned} \tag{2}$$

The relative ionic yield of CF_3^+ and CF_2H^+ is described by

$$J_{CF_3} = \frac{P_{CF_3}}{P_{CF_3} + P_{CF_2H}} \quad \text{and} \quad J_{CF_2H} = \frac{P_{CF_2H}}{P_{CF_3} + P_{CF_2H}} \tag{3}$$

or

$$J_{CF_3} = \frac{N_F}{N_F + 3N_H} \quad \text{and} \quad J_{CF_2H} = \frac{3N_F}{N_F + 3N_H} \tag{4}$$

Having considered that for copolymer of trifluorethylene with ethylene $N_F=N_H$, then we get $J_{CF3}=0.25$; $J_{CF2H}=0.75$. Similarly, it is possible to determine the relative ionic yields of CF_3^+ and CF_2Cl^+ from (poly) trifluorethylene.

$$J_{CF_3} = \frac{P_{CF_3}}{P_{CF_3} + P_{CF_2CL}} \quad \text{and} \quad J_{CF_2Cl} = \frac{P_{CF_2Cl}}{P_{CF_3} + P_{CF_2Cl}} \tag{5}$$

or

$$J_{CF_3} = \frac{N_F}{N_F + 3N_{Cl}} \quad \text{and} \quad J_{CF_2Cl} = \frac{3N_F}{2N_F + 3N_{Cl}} \tag{6}$$

Then [13] considering that N_F: N_{Cl}=2:1, discover J_{CF3}=0.4 and J_{CF2Cl}=0.6. Thus, the relative ionic yield of CF_3^+ and CF_2H^+ in copolymer makes 25% and 75% from entire their current, and CF_3^+ and CF_2Cl^+ in (poly) trifluorethylene makes 40 % and 60% from entire currents CF_3^+ and CF_2C^+. The results of the relative yield calculation of these ions along of all four mechanisms are given in the table below. It is also reflected the experimental outputs in the same table on the bottom row.

It is observed from the table that the experimental values of the relative ionic yields of CF_3^+ and CF_2H^+ well correlate with rated on the mechanism 1 and to the mechanism 4. Appropriate values of ions CF_3^+ and CF_2Cl^+ well correlate with rated on mechanisms 2 and 4. Thus, it is possible to state that the 4th mechanism is responsible in the formation of these ions, which provides affixing the atoms of H and Cl to CF_2^+ irrespective of the location of molecules CH_2 or CCl_2 (Table 1).

The absence or small contribution of ion-molecule reaction (the mechanisms 1 and 2) in the processes of ions CF_3^+ and CF_2H^+ or CF_2Cl^+ formation, can be explained with high packing density of CH_2 or CCl_2 molecules around a carbonic chain which interfere with processing of reaction [12]. Indeed, ionic fragments of $CF2^+$, CFH^+ and $CFCl^+$ at the bombing gain so major portion of energy that the difference in binding energies is not played any role. Connection is broken almost with equal probability and at linking of this or that atom to a fragment in the core is spotted by their density in carbonic chains.

For explanation of mechanisms of secondary ions formation from a solid body surface, the various models were offered; according to them the primary ions (atoms) interacting with a target surface, cause a series of collisions which being spread on a solid body transmitting the moment of movement to atoms of the substance. Some of excited near-surface atoms having gained the moment of movement are directed to a surface can overcome binding forces with it and depart to a vacuum with energy of several electron volts. The regularity of an atom yield from metals is described by the theory of cathode sputtering [8].

However, it is difficult to suggest that the regularity for the second - ion emission characteristic for metals will validly for the molecular dielectrics as well. Indeed, metal consists of the same sort of atoms coupling equally with each other; but in the molecular dielectric atoms of different type are related among themselves by various types of chemical bonds, i.e. aggregated in molecules between which in turn are available more feeble intermolecular interaction. Further, there are no free electrons in dielectrics; which presence in the metals sharply reduces probability of secondary ions yield. Bombarding radiation by a flow of accelerated particles causes fracture of a crystal lattice of metal, and in the molecular dielectric, besides a change of permolecular structure of the sample, it is also possible non reversible chemical transformations.

For understanding of secondary ions formation mechanisms from the molecular substances, a major role have played the investigations of the ionic clusters being formed by activity of accelerated particles (or laser radiation) on local field of a surface. The mechanism of formation of the ionic clusters at the bombing of a dielectric film by accelerated atoms (in our case of argon), it is possible to introduce as follows [10, 11]. At corpuscle impact to a target, there is a heat-up of a small section of a surface with a diameter about 10 nanometres is taking a place. In a central part of a hot spot dielectric

can be warmed up to such degree that molecular bonds, being typical for a solid body, can be destructed and the substances in this field can be considered as very dense ionisation gas.

The investigations of the mechanism of excitation and dissociation of polyatomic ions formed in the dense plasma and being in thermodynamic equilibrium [2] have shown that process of a dissociation of a molecular ion carries out on two stages: at the first stage there is a molecular ion excitation as uniform molecular system, and then the excited ion collapses on fragments. According to authors [12] such process will occur if $\tau_g>\tau$, where τ_g - excited ion lifetime, τ - lifetime of system from facing corpuscles. If keep in mind that the greatest prompt dissociative processes carries out during 10^{-13} sec, and lifetime of the majority raised consisting atoms are 10^{-10} - 10^{-8} sec, then the requirement performance $\tau_g>\tau$ does not cause doubts.

Table 1. Rated and experimental values of secondary ions relative yields

Mechanism	CF_3	CF_2H	CF_3	CF_2Cl
1	0,25	0,75	0,5	0,5
2	0.5	0.5	0.4	0,6
3	0.5	0,5	0,25	0,75
4	0,25	0.75	0.4	0.6
Experimental outputs	0.26 ± 0.02	0.75 ±0.01	0.41 ± 0.008	0.59 ± 0.02

IV. CONCLUSIONS

It was used quasi-equilibrium model [4] for description of the mechanism of secondary ions formation at the analysis of the molecular dielectric, according to which, secondary ions are formed at the centres of a local heating of a surface. Particularly at these heating centres atoms interchanging processes occurs between the ionic fragments and neutral molecules of the polymer. There are 4 possible mechanisms [7] of interchanging including as ion-molecular reactions (mechanisms 1 and 2), and regrouping processes (mechanisms 3 and 4).

The paper discussed about Carried out calculations of the relative yields of secondary ions in a mass spectrum of all four mechanisms and their comparison with the experimental results found to refer them to appropriate mechanisms of ion formation.

The experimental results found to make conclusion about physical-chemical parameters influences of elements on their relative yields (and to mean the formation mechanism) of secondary ions.

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BIOGRAPHIES

Zulfugar (Kamil oglu) Nurubeyli was born in Azerbaijan on 06.05.1976. He graduated from Azerbaijan State Oil Academy (Baku, Azerbaijan) in 2001 and received the Master degree in Honors. Since 2006 he is the candidate of physics-mathematical sciences and engaged in development and further improvement of analytical abilities of mass-spectrometer. He has over 30 publications in Azerbaijan and abroad, also is author and coauthor of several inventions as well as participated in several international conferences.

Kamil (Zulfugar oglu) Nuriyev was born in Azerbaijan on 03.09.1939. He is the candidate of physico-mathematical sciences and chief researcher of laboratory "physics and techniques of high voltages". He engaged in development, production and investigation of time of flight mass-spectrometers for more than 20 years. He has over 50 publications in Azerbaijan and abroad, also he is author and coauthor of 6 inventions. The analyzer with axial-symmetric electric field is developed under his leadership and successfully used for determining element and isotope composition of condensed phases.

Kamil (Bakhtiyar oglu) Gurbanov was born in Azerbaijan on 09.12.1942. He is candidate of physical and mathematical sciences and deputy director of Institute of Physics, Azerbaijan National Academy of Sciences (Baku, Azerbaijan). He is engaged in studying of an ecological state of environment, detection and recycling of gases and steams - emissions in the industry; water reservoir refinement, development and realization of effective methods and cleaning installations for more than 20 years. He is the holder of more than 10 invention patents.

Tarana (Kamil qizi) Nurubeyli was born in Azerbaijan on 17.02.1979. She graduated from Baku State University (Baku, Azerbaijan) in 2001 and received the Master degree in Honors. Since 2004 she is the research assistant of Institute of Physics, Azerbaijan National Academy of Sciences (Baku, Azerbaijan). Her scientific interest are design of mass analyzers, estimation of assembly and designing of time of flight energy-mass analyzers, carrying out of tests of developed devices, planning and carrying out of scientific researches with a chromatograph mass spectrometer. At the present, she prepares for the Ph.D. thesis defense on a theme "energy-mass analyzer of the charged particles with axial-symmetric electric field".

Anvar (Teymur oglu) Khudiev was born in Fizuli, Azerbaijan on January 5, 1938. He received the M.Sc. degree from Azerbaijan State University (Baku, Azerbaijan) in 1961, the Ph.D. degree from Institute of Organic Chemistry Academy of Science (Moscow, USSR) in 1967 and Doctor of Science from Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences (Baku, Azerbaijan) in 1989 in Chemical Engineering and Zeolites. Currently, he is the Full Professor in Institute of Petrochemical Processes (Baku, Azerbaijan). His research interests are in Physical Chemistry, Kinetics and Catalysis, Separation Processes, Water Treatment, Adsorbents, Synthetic and Natural, Zeolites, Environmental Protection. He published more than 200 papers in international conferences and journals and has also 21 patents.