International Journal of Mass Spectrometry 286 (2009) 11–16

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Surface characteristics of glass fibres covered with an aluminum layer after a chemical modification process using secondary ion mass spectrometry (SIMS) and atomic force microscopy (AFM)

Katarzyna Kupiec[a,*], Piotr Konarski[b], Piotr Konieczka[a], Jacek Namieśnik[a]

[a] Chemical Faculty, Department of Analytical Chemistry, Gdansk University of Technology, Narutowicza St. 11/12, 80-952 Gdansk, Poland
[b] Tele and Radio Research Institute, Ratuszowa 11, 03-450 Warszawa, Poland

ARTICLE INFO

Article history:
Received 10 April 2009
Received in revised form 4 June 2009
Accepted 8 June 2009
Available online 26 June 2009

Keywords:
Matrix-less reference material
Certified reference material
Pyrolysis
Atomic force microscope
Secondary ion mass spectrometry

ABSTRACT

Results show investigations of surface of modified glass fibres (before and after chemical modification of their surface), which are candidates for future original matrix-less reference material for volatile ethene analytes (C_2H_4). Used analytical methods are secondary ion mass spectrometry and atomic force microscopy. The investigations were aimed at observation of changes and processes which occurred on the surface of glass fibres covered with an aluminum layer and constituting an ethane carrier.

The paper describes the procedure of chemical modification of the surface of 3 cm segments of glass fibres covered with an aluminum layer (660/680 μm, external diameter of quartz/external Al diameter), a surfactant constituting a source of ethene. Ethene (a measured constituent) in a standard gas mixture is obtained during the process of controlled thermal decomposition of a surface compound in a stream of rarefied gas (such kind of mixture is called matrix-less reference material).

1. Introduction

Since many years the Chemical Faculty, Chair of Analytical Chemistry of Gdansk University of Technology carries out research on creation of a new genuine matrix-less reference material for volatile analytes, using the technique of gas chromatography linked with thermal desorption (GC-TD). Now we succeeded in obtaining a candidate for a future reference material, available commercially (Cezar International Group, Photonics Technology) glass fibre covered with an aluminum layer in order to increase the mechanical strength of this material. Fibres modified in such way constitute a carrier of a surfactant being a source of ethene (C_2H_4) [1,2]. The amount of ethene released from sections of chemically modified glass fibres, after 9 min of thermal dissociation pyrolysis (temperature 280 °C) equals 0.767 ± 0.083 ng/cm.

The process of obtaining ethene (as a measured constituent) in a gaseous standard mixture is based upon the use of surfactants, chemically bounded with the surface of the carrier, which at specific temperatures undergo thermal destruction or chemical rearrangements accompanied by release of precisely defined amounts of volatile analyte. The released compounds are subsequently washed out from the reaction chamber (chromatograph dispenser, thermal desorber) by means of a stream of rarefied gas, forming a jet of gaseous standard mixture (such type of mixture is called a matrix-less reference material).

It was decided to characterize the surface of new type glass fibres forming the carrier of an appropriate compound which can be a source of ethene in a controlled pyrolysis process. In the investigations the techniques of Secondary Ion Mass Spectrometry and Atomic Force Microscopy were used. These investigations were performed to observe changes and processes present at the surface of the carrier.

2. Experimental

2.1. Fabrication of a surface compound being the source of ethene

The procedure of modifying the surface of a carrier in order to form a surface compound being the source of ethene has been patented earlier and made use of already [1]. It was used to modify the surface of only one carrier—silica gel (with a specific surface of 200 m^2/g).

The process of chemical modification of the carrier's surface is carried out in the Chemical Faculty, Chair of Chemical Technology of Gdańsk University of Technology. Glass fibres covered with a thin layer of aluminum (Fig. 1) were dried at a temperature of 120 °C for 8 h in order to remove adsorbed water. A sample of the carrier thus prepared was placed in a flask containing 60 ml of toluene. Then

* Corresponding author.
E-mail address: kasia.k177@wp.pl (K. Kupiec).

1387-3806/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2009.06.009

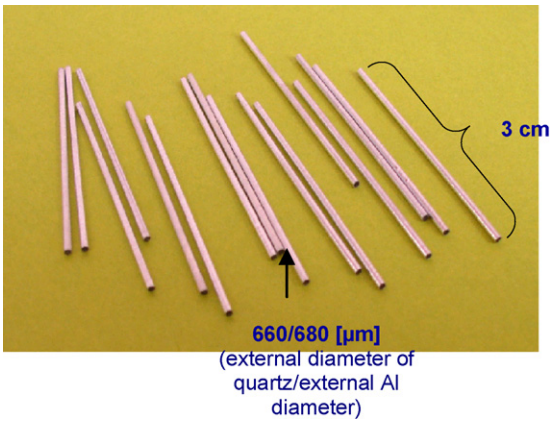

Fig. 1. Glass fibres covered with a layer of aluminum, after a process of chemical modification leading to the creation of a surfactant which can be a source of ethene in a controlled pyrolysis process.

0.025 mol of (3-chloropropylo)-trimetoxysilane was added to the solution. The reaction was carried out for 6 h at 80 °C. The silanized carrier obtained from the reaction was filtered off and washed in turn with toluene, methyl alcohol and acetone and subsequently dried in vacuum. The obtained product was flooded with toluene (60 ml) and 0.025 mol of dimethylamine. Then the solution was heated at 80 °C for 6 h. After completing the reaction, the product was again filtered off, washed and dried in vacuum. In the next synthesis step 10 ml of 30% H_2O_2 was added. The obtained batch of the product with modified surface was accurately washed and dried.

Fig. 2 presents a scheme of the synthesis of the surfactant constituting a source of ethene obtained (in a controlled pyrolysis process) as a measured constituent of an appropriate gaseous standard mixture [2].

2.2. Secondary ion mass spectrometry

The investigation was carried out using the technique of secondary ion mass spectrometry (SIMS) [3–6]. The subject of research were sections of glass fibres of 3 cm length, covered with an aluminum layer, commercially available (Fig. 1)—unmodified and after a process of modification with a surfactant constituting a source of ethene, which was described in detail in Section 2.1. The glass fibres were placed on a measuring stand in sets of seven pieces.

The investigation was carried out with the use of SIMS spectrometer SAJW-05 model [7]. The operating parameters were as follows:

- Primary ion beam: 2 keV, Ar^+.
- Primary beam raster: 0.11 cm^2.
- Ion gun – 06-350 E Physical Electronics.

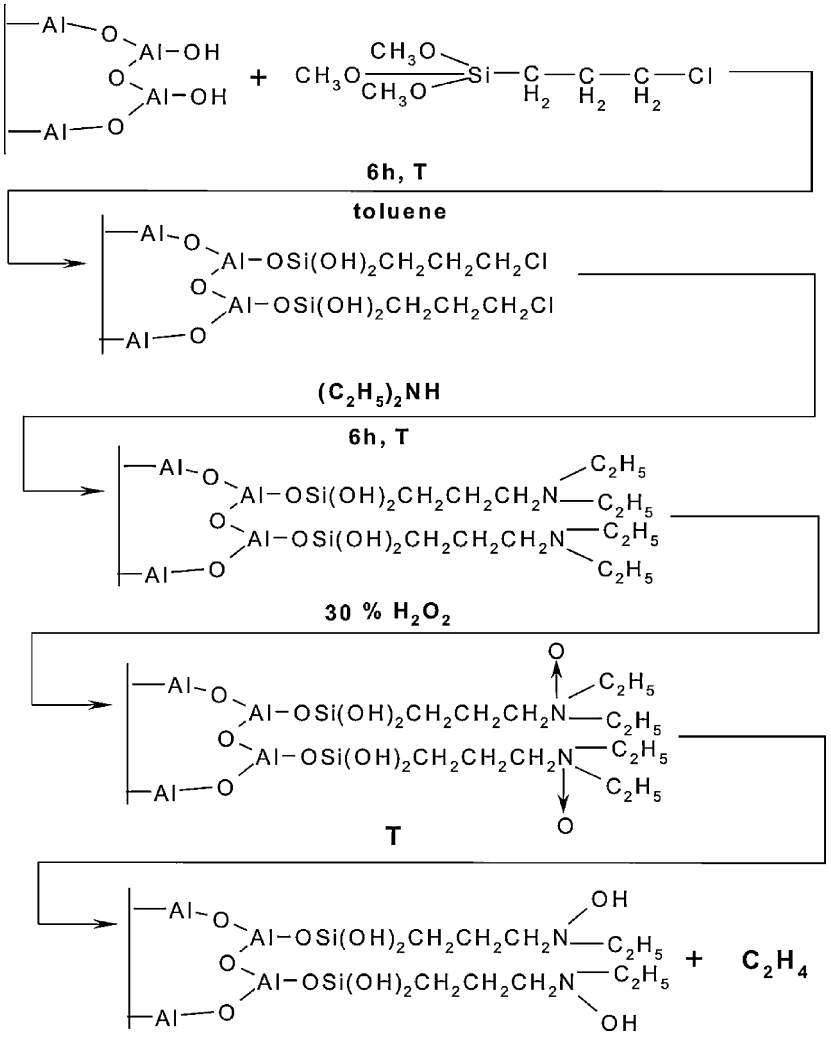

Fig. 2. Diagram of the synthesis of a surfactant on the surface of a carrier and of its thermal decomposition (in a stream of carrier gas) with release of ethene (during a controlled pyrolysis).

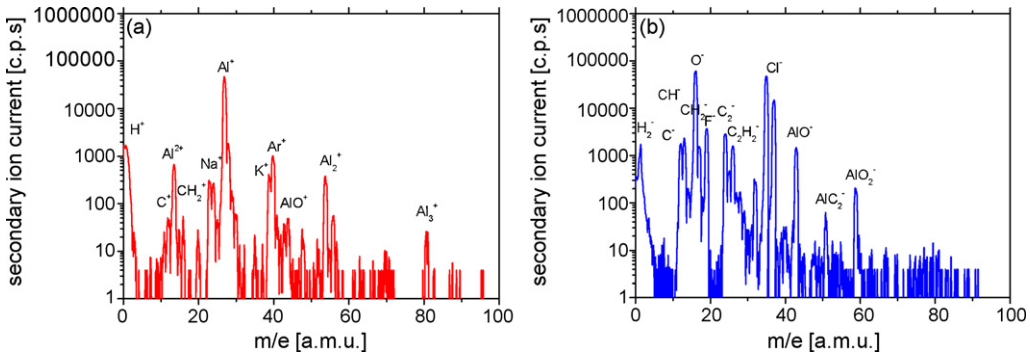

Fig. 3. Secondary ion mass spectrograms of (a) positive and (b) negative ions, obtained during 2 keV Ar^+ ion beam bombardment of glass fibres covered with an aluminum layer, after a process of chemical modification of their surface with a surfactant constituting a source of ethane.

- Quadrupole mass analyzer – QMA 410 Balzers.
- Depth profile analysis of positive primary ions: H^+, H_2^+, C^+, CH_2^+, Al^+ and negative secondary ions: H_2^-, C^-, CH^-, CH_2^-, C_2^-, AlO^-, $C_2H_2^-$ and AlC_2^-.

2.3. Atomic force microscopy

The characteristics of glass fibres covered with an aluminum layer after a process of modification of its surface were obtained by the method of atomic force microscopy (AFM) [8–10] with the use of a NTGRA Prima equipment from NT-MDT; this measurement was carried out in the Chemical Faculty, Chair of Electrical Chemistry, Corrosion and Materials Engineering of Gdańsk University of Technology.

To observe the effect of the modification by a surfactant constituting a source of ethene on the surface of glass fibres covered with an aluminum layer, imaging by the AFM technique in contact mode was used (Figs. 8 and 9).

The analysis included two kinds of fibres covered with a layer of aluminum (external diameter of quartz/external diameter of Al) 660/860 (μm):

- fibres before the chemical modification process;
- fibres after a process of chemical modification with a surfactant constituting an ethene source.

These investigations were conducted in an air atmosphere and at room temperature.

3. Results and discussion

3.1. The use of the SIMS technique for characterizing the carrier after modification of its surface in a chemical process

Fig. 3 presents examples of secondary ion mass spectrograms for positive and negative ions (obtained with the SIMS technique) for sample after the modification process.

Depth profile analysis was carried out for selected secondary ions. The obtained results were normalized. Sputtering time has been converted into depth under the assumption that the sputtering rate of outer atomic layers in aluminum is similar to that in tantalum oxide Ta_2O_5 in a test sample of 10 nm Ta_2O_5/Ta. The obtained sputtering rate was 1.4 nm/min due to 0.11 cm^2 primary beam raster area. The result of the test sample analysis is shown in Fig. 4.

Figs. 5–7 show the relative values of currents of individual secondary ions. The ratio of these currents to the value of the emission current I_{bulk} measured in the bulk aluminum. The assumption has been made, that after etching away a layer of about 20–30 nm, the composition of the etched material – aluminum – is already similar to that of bulk aluminum. Normalization of this kind allows to become independent of such factors as surface topography, matrix effects and other effects which affect the total emission of secondary ions from the bombarded surface. This kind of normalization also permits to notice changes in the emission of secondary ions in the course of ion etching of the upper atomic layers of the investigated material.

3.2. Utilization of the AFM technique for the characterization of a carrier after the process of chemical surface modification

3.2.1. The effect of modification of glass fibres covered with an aluminum layer on the appearance of that surface, obtained in the result of using atomic force microscopy

Figs. 8 and 9 present the results of observation of changes which occurred on the surface of tested samples before and after the process of chemical modification with a surfactant constituting a source of ethene.

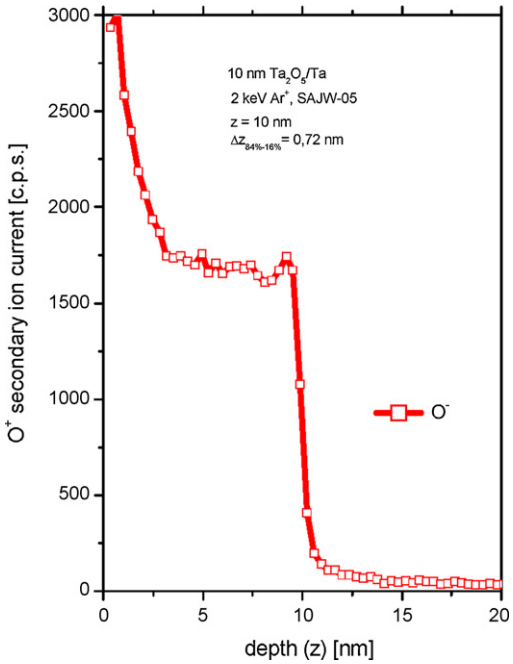

Fig. 4. Result of depth profile analysis of 10 nm thick Ta_2O_5 layer obtained by electrolysis of the tantalum surface. High oxygen secondary ion current measured at the initial stage of depth profile (up to 3 nm) is caused by oxygen contamination on tantalum oxide surface or other contamination enhancing O^+ emission. The obtained depth profile resolution $\Delta z_{84-16\%}$ at oxide/metal interface is 0.72 nm.

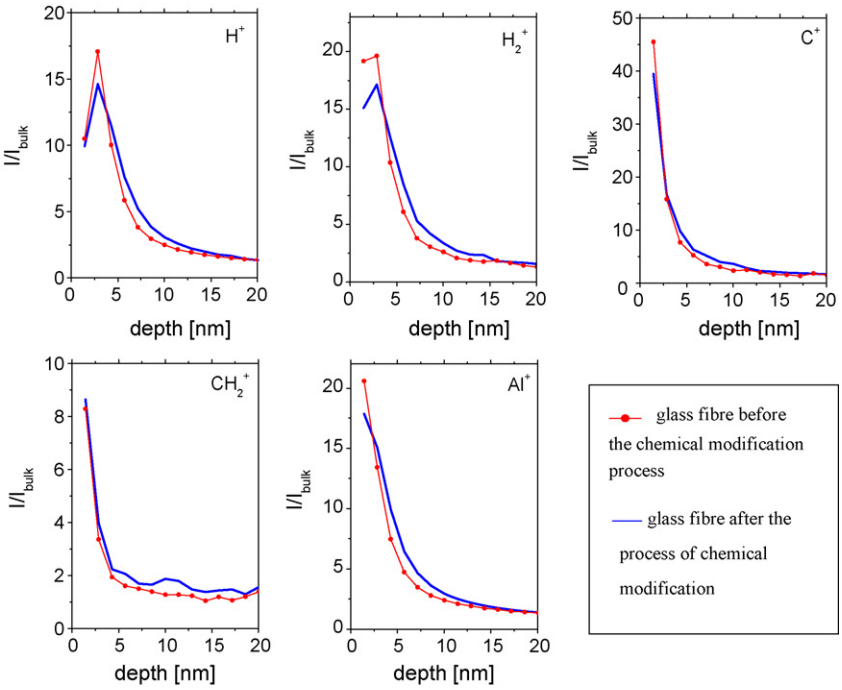

Fig. 5. Depth profile analysis of surface layers of glass fibres. Emission of positive secondary ions H^+, H_2^+, C^+, CH_2^+, Al^+ was monitored.

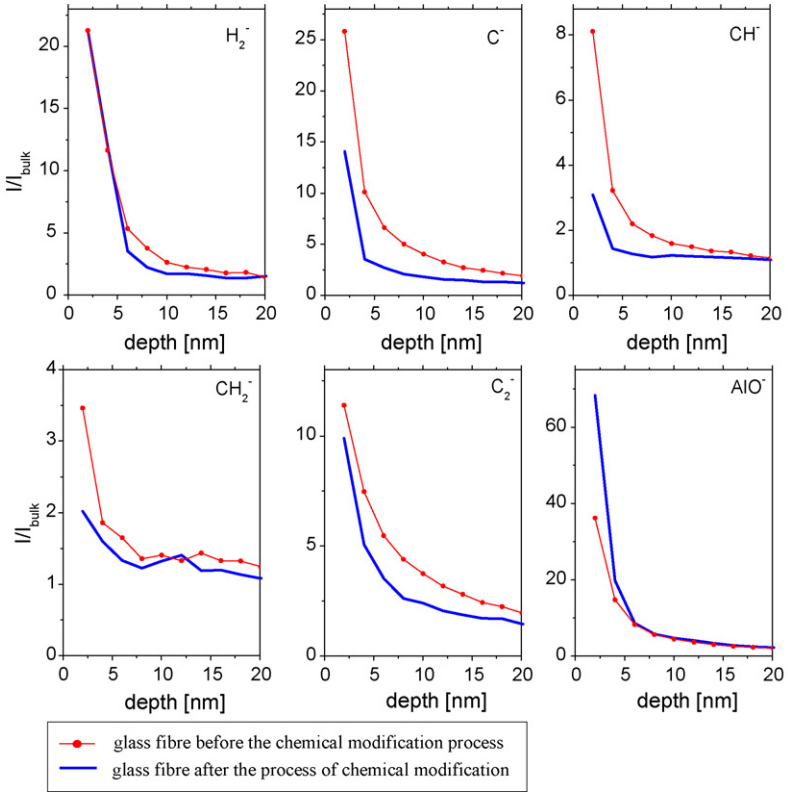

Fig. 6. Depth profile analysis of surface layers of glass fibres. The analysis includes negative secondary ions H_2^-, C^-, CH^-, CH_2^-, C_2^-, AlO^-.

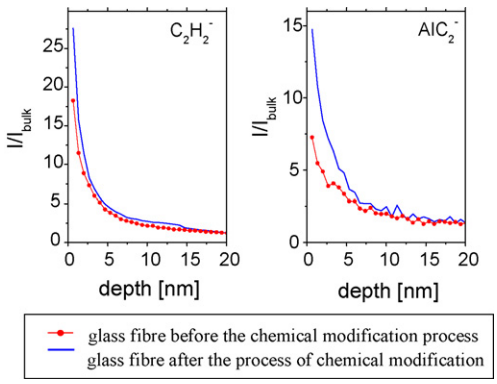

Fig. 7. Depth profile analysis of surface layers of glass fibres. The analysis includes negative molecular secondary ions $C_2H_2^-$, AlC_2^-.

Fig. 8 presents the appearance and irregularity heights on the surface of tested samples before and after the chemical modification process. It is evident that the process of chemical modification of glass fibres covered with an aluminum layer constituting a source of ethene leads to an increase in inhomogeneity and of height irregularities. For unmodified samples the irregularities are between 1 and 12 nm (Fig. 8a), while for modified samples the irregularities are between 1 and 50 nm (Fig. 8b).

3.2.2. Determination of parameters characterizing the interaction force of the scanning probe with the surface of glass fibres before and after the chemical modification process

AFM microscopy, besides imaging a surface, permits also to measure accurately the forces of interaction of the scanning probe with the surface of the investigated surface [11–14].

The interaction forces have been measured between the surface of glass fibres covered with aluminum, before and after the process of chemical modification, and the moving scanning probe. Fig. 10 presents the obtained exemplary relationship between the moving scanning probe and the surface of glass fibres. On the basis of these diagrams it was possible to determine the force of interaction F (adhesion force) from the deflection of the scanning probe lever in relation to the scanned surface according to Hooke's law [8,9]:

$$F = k \cdot \Delta H \ \text{(N)}$$

where k – elasticity constant of the lever (0.03–0.2) (N/m); ΔH – distance between the scanning needle and the sample surface (nm).

The results of interaction forces between the scanning probe and the surface of glass fibres allow to state that the adhesion force is greater for glass fibres before the chemical modification process and is 48.25 nN, but for fibres after the process of modification with a surfactant being a source of ethene the adhesion force is 28.35 nN.

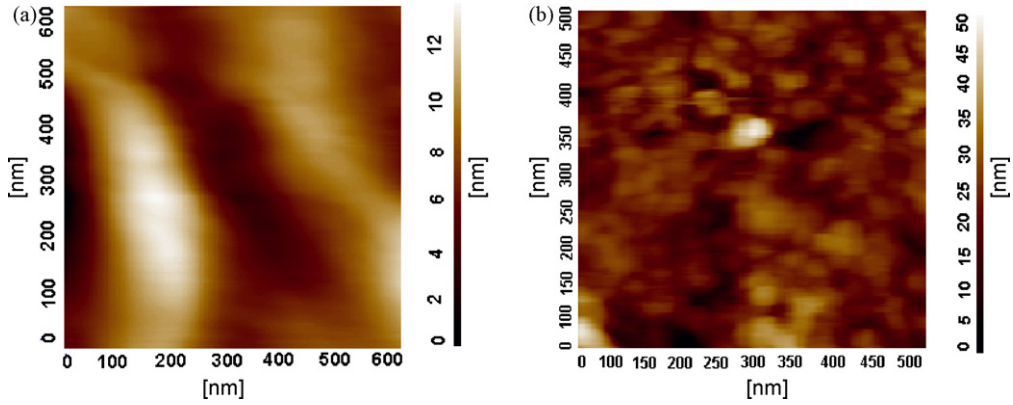

Fig. 8. Images obtained with the use of AFM, showing the heights of irregularities on the surface of glass fibres covered with an aluminum layer: (a) before the process of chemical modification; (b) glass fibre after chemical modification by means of a surfactant constituting a source of ethane.

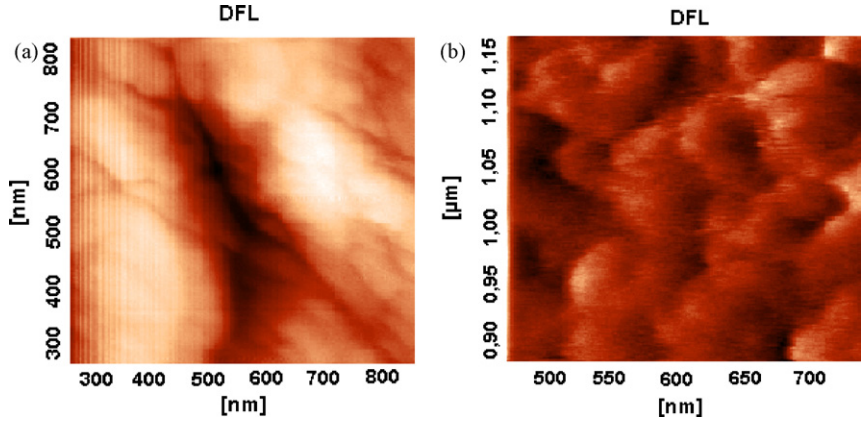

Fig. 9. Differential images (DFL) in the x–y plane of glass fibres covered with an aluminum layer, obtained with an atomic force microscope: (a) fibre before the chemical modification process; (b) fibre after the process of chemical modification by means of a surfactant constituting a source of ethane.

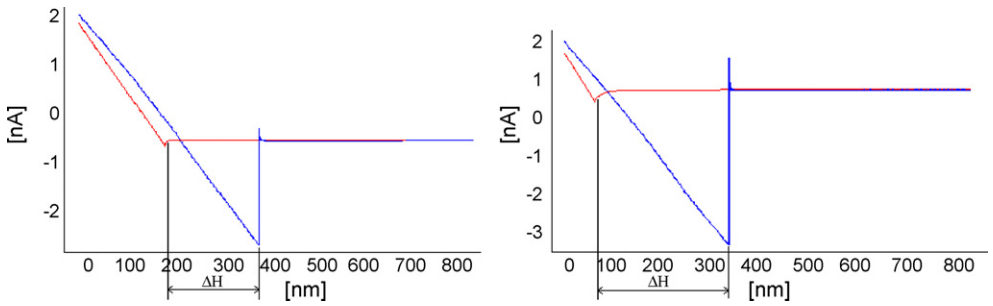

Fig. 10. Diagrams presenting the (lever deflection) forces depending on the distance of the scanning needle with respect to the surface of the tested sample: (a) fibres before the process of chemical modification; (b) fibres after the process of chemical modification by means of a surfactant constituting a source of ethane.

4. Conclusions

On the basis of investigations conducted with the use of SIMS it has been found that carrying out the modification process of the surface of glass fibres covered with an aluminum layer with a surfactant constituting a source of ethene, causes a change of the elemental composition of the upper layer of aluminum (emission of negative secondary ions is explicitly lower). It has been found that the upper layer of fibres covered with an aluminum layer, after the modification process is probably impoverished by some impurities existing on the fibres before modification. Many different ions are characterized by higher emission from the surface of samples before the modification. From among the investigated secondary ions only ions $C_2H_2^-$ and AlC_2^-, i.e., ions containing the bond C–C (or C=C) show higher emission from the upper layer of samples after the modification process. This fact indicates that there exist ethene molecules or their fragments on the surface of glass fibres covered with a layer of aluminum.

The obtained results of depth profile analysis of the surface of glass fibres which are not ethene carriers show an explicit presence of typical impurities on the surface of aluminum, containing such elements like hydrogen, carbon and oxygen. The presence of these impurities may affect the increased emission of negative secondary ions. This is a typical effect often observed during investigations carried out with use of the SIMS technique. The presence of impurity elements and oxygen in the aluminum layer increases the emission of secondary ions.

The tests have disclosed essential differences in the composition of surfaces of unmodified glass fibres and those constituting a source of volatile ethene analytes. It has been demonstrated that the surfaces of unmodified fibres contain more impurities composed of carbon and hydrogen than surfaces of fibres modified by means of a surfactant being a source of ethene. It has been also shown that the emission of selected negative secondary ions containing two carbon atoms is higher during the etching process of surfaces modified with a surfactant constituting a source of ethene. This testifies the presence of ethene on these fibres in comparison with unmodified fibres.

The investigations indicate that treatment of the surface of aluminum with a surfactant which is a source of ethene (in a pyrolysis process) not only leads to its modification but also removes from this surface other impurities, e.g., hydrocarbons.

The results of analyses obtained with the use of the AFM technique indicate that the process of chemical modification of glass fibres covered with an aluminum layer by means of a surfactant constituting a source of ethene explicitly affected the change of the surface structure of this material by increasing its inhomogeneity and roughness (Figs. 8 and 9). Besides, the measurement of interaction forces with the method of atomic force microscopy indicates that glass fibres subjected to chemical modification are characterized by lower adhesion force of the scanning needle to the scanned surface.

References

[1] A. Świtaj-Zawadka, A. Naganowska-Nowak, P. Konieczka, J.F. Biernat, J. Szczygielska-Tao, J. Namieśnik, Trends Chromatogr. 1 (2005) 71–75.
[2] A. Naganowska-Nowak, P. Konieczka, J.F. Biernat, J. Szczygielska-Tao, A. Przyjazny, J. Namieśnik, Anal. Bioanal. Chem. 388 (2007) 1725.
[3] R.G. Wilson, F.A. Stevie, Ch.W. Magee, Secondary Ion Mass Spectrometry—A Practical Handbook for Depth Profiling and Bulk Impurity Analysis, John Wiley & Sons Inc., New York, 1989.
[4] J.M. Walls, Methods of Surface Analysis—Techniques and Applications, Cambridge University Press, Cambridge, 1989.
[5] E.H. Cirlin, J. Vajo, T.C. Hasenberg, R.J. Hauenstein, High resolution secondary ion mass spectrometry depth profiling using continuos sample rotation and its application to superlattice and delta doped sample analysis, J. Vac. Sci. Technol. A8 (1990) 4101.
[6] S. Hofmann, Compositional depth profiling by sputtering, Prog. Surf. Sci. 36 (1991) 35.
[7] P. Konarski, A. Mierzejewska, B_4C/Mo/Si and Ta_2O_5/Ta nanostructures analysed by ultra-low energy argon ion beams, Appl. Surf. Sci. 203–204 (2003) 354–358.
[8] D. Sarid, Scanning Force Microscopy, Oxford University Press, New York, 1991.
[9] R. Wiesendanger, Scanning Probe Microscopy and Spectroscopy: Methods and Applications, Cambridge University Press, Cambridge, 1994.
[10] T. Eastman, D.M. Zhu, Adhesion forces between surface-modified AFM tips and a mica surface, Langmuir 12 (1996) 2859–2862.
[11] J. Drelich, G.W. Tormoen, E.R. Beach, Determination of solid surface tension from particle–substrate pull-off forces measured with the atomic force microscope, J. Colloid Interface Sci. 12 (2004) 484–497.
[12] M.D. Louey, P. Mulvaney, P.J. Stewart, Characterisation of adhesional properties of lactose carriers using atomic force microscopy, J Pharm. Biomed. Anal. 25 (2001) 559–567.
[13] Q. Ouyang, K. Ishida, K. Okada, Investigation of micro-adhesion by atomic force microscopy, Appl. Surf. Sci. 169–170 (2001) 644–648.
[14] E.-S. Yoon, S. Ho Yang, H.-G. Han, H. Kong, An experimental study on the adhesion at a nano-contact, Wear 254 (2003) 974–980.