

GDOES AND GDMS ANALYTICAL SYSTEMS, EFFECTIVE TOOLS FOR CHARACTERIZATION OF CONDUCTIVE AND NONCONDUCTIVE MATERIAL SURFACES

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In this paper we present GDOES and GDMS analytical methods, the identification and the distribution along the polymer thickness of different compounds generated during the polymerization process occurred in corona discharges starting from liquid precursors. Also, analyzing by GDOES technique the metallic samples, copper and brass implanted with nitrogen we have successfully evidenced the efficiency of a new, original, processing plasma which is 10 times denser than conventional low pressure plasma.

Keywords: GDOES, GDMS, surface plasma processing.

1. Introduction

Glow Discharge Optical Emission Spectrometry (GDOES) and Glow Discharge Mass Spectrometry (GDMS) are powerful techniques for high resolution depth profiling analysis of a variety of materials including conductive and non-conductive thin layers. The standard plasma source of these analytical systems is the Grimm cell, the sample being the RF electrode located in front of the anode cavity. The processes associated to this kind of discharges and their analytical aspects has been previously approached [1-10].

In our previous papers [11-15] we presented the results obtained by GDOES and GDMS methods which were successfully used for chemical identification and depth profiling analysis of the polymers obtained in corona discharges starting from organic and organosiliconic liquid precursors [11,16-18]. The distribution of the chemical elements along the polymer thickness, generally the oxides generated during the polymerization process were identified, using the

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GDOES depth profile technique, at the surface, on the polymer/substrate interface or in the polymer bulk. The existence of different kinds of compounds was anticipated by the Infrared Spectroscopy (IR), X-Ray Photoelectrons Spectroscopy (XPS) or Energy Dispersive Spectroscopy (EDS) measurements previously reported [19, 20].

The GDOES analysis successfully evidenced the efficiency of ion implantation and deposition on metallic and non-metallic surfaces by immersion in a new type of processing plasma. The new type of plasma consists of RF modulated discharges obtained by applying supplementary HV pulses under RF field so that the negative pulse applied on the target find a background plasma about 10 times denser than conventional low pressure plasma (10^{10} cm^{-3}) [21].

2. Results and discussions

The procedure of polydimethylsiloxane (PDMS) layer generation in corona discharges in air at atmospheric pressure starting from liquid precursors was presented in details in [11-20].

The depth profiles analysis of the PDMS polymers was done by Glow Discharge Optical Emission Spectrometry (GD OES) and Glow Discharge Time of Flight Glow Discharge Mass Spectrometry (GD-TOFMS).

By these techniques an area of 4 mm of the polymer layer is sputtered in a pulsed RF Ar plasma. The sputtered atoms from the polymer are then excited by inelastic collisions in the plasma and the emitted light is monitored in real time providing the elemental composition of the polymer sample as a function of the depth in layer. The GD OES used in the experiment was a GD Profiler 2 from Horiba Jobin Yvon. The selected operating conditions were: 650 Pa for pressure and 25 W RF power, working in pulsed mode at 3 kHz pulsing frequency and a duty cycle of 0.25 [11].

By GD-TOFMS technique species sputtered and ionized in the Ar RF plasma are directed to a mass spectrometer. The experimental conditions used for the polymers analysis in PP-TOFMS were: 700 Pa pressure and 30 W Rf power working in pulsed mode. The pulse duration was 1 ms and the period 4 ms. Mass spectra are recorded on the entire pulse duration and thereby in the afterglow plasma. Signals of investigated ions exhibit a considerable intensity enhancement when the RF pulse is turned off, in the afterglow of the pulsed RF plasma. In the specific case of polymer-based films it was found that the afterglow regime is important as it mostly contains fragment ions that could be related to the polymer [11].

The Si, C, O, H and Al depth profile curves obtained by the GDOES and GD-TOFMS techniques are presented in Figure 1. differ for Ti and Al substrates. The peaks on Si and O depth profiles show the silicon oxides structures formation

at polymer surface. The fact that C and H present similar depth profiles means that C and H atoms are linked to silicon oxides structures. The steep rise in the aluminum depth profile curve and the decreasing of the Si, O, C, and H signals indicates the polymer/substrate interface.

In Fig. 1a, at the polymer - Al interface, one can observe a hump on the O depth profile curve. There are not such humps on the Si, C, and H depth profiles. The change of sputtering rates from layer to layer characteristics of GD-OES multilayer analysis cannot simply explain this phenomenon which can on the other hand be an indicator of the presence of Al oxides at the polymer/Al substrate interface. Also, one can observe that there is a simultaneous increase of the oxygen and aluminum signals during the decreasing of the Si depth profile curve. Due to the roughness of the aluminum oxide layer formed at the polymer substrate interface the ending point of the polymer layer cannot be exactly established.

Similar depth profile curves of the PDMS layer components were obtained by GD-TOFMS technique, Fig. 1b.

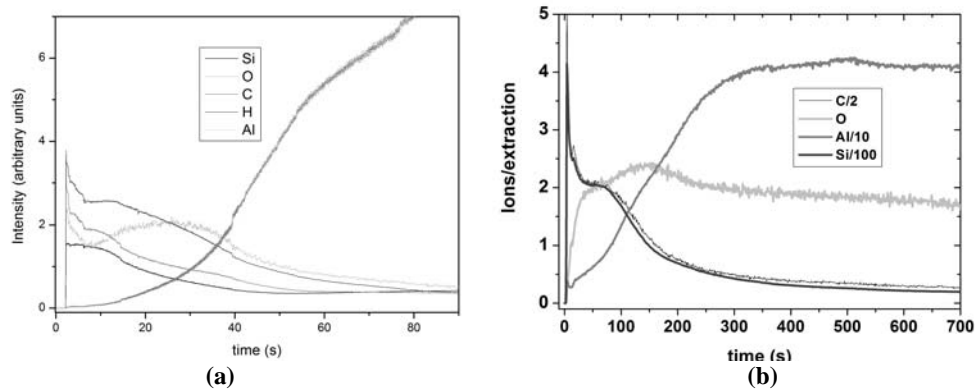


Fig. 1. Elemental depth profile of the polymer layer deposited in corona discharges on Al substrate by: a) GDOES; b) GD-TOFMS technique.

Fig. 2 shows the mass spectrum recorded in the afterglow of the pulsed RF plasma. It can be identified the formation of Al_2O_3 compounds. Because in the pulsed RF plasma a lot of chemical bonds are broken, especially those with hydrogen, we will have a lot of byproducts. Thus, due to H addition, these aluminum oxides based compounds are observed in the mass spectrum as $\text{Al}_2\text{O}_3\text{H}^+$ (m/z 102.9), $\text{Al}_2\text{O}_3\text{H}_2^+$ (m/z 103.9), $\text{Al}_2\text{O}_3\text{H}_3^+$ (m/z 104.9), $\text{Al}_2\text{O}_3\text{H}_4^+$ (m/z 105.9), $\text{Al}_2\text{O}_3\text{H}_5^+$ (m/z 106.9), $\text{Al}_2\text{O}_3\text{H}_6^+$ (m/z 107.9), $\text{Al}_2\text{O}_3\text{H}_7^+$ (m/z 108.9). The fragments like $\text{Al}_2\text{Si}_2\text{O}^+$ (m/z 125.9 m/z), $\text{Al}_2\text{Si}_2\text{OH}^+$ (m/z 126.9), $\text{Al}_2\text{Si}_2\text{O}_2^+$ (m/z 141.9) possible indicate the formation of aluminosilicates type compounds ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) at polymer/substrate interface. These signals appear in the recorded mass spectrum only on the duration of the aluminum temporal profile.

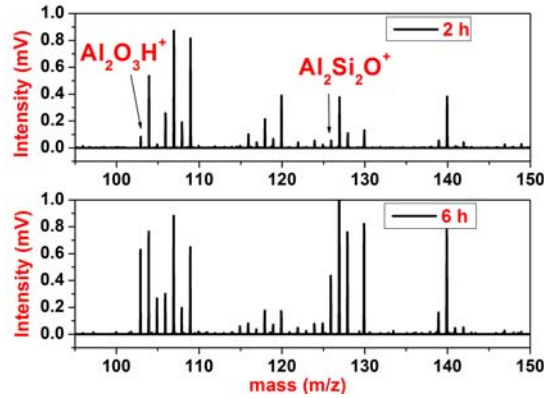


Fig. 2: Mass spectrum of compounds obtained at polymer/substrate interface for 2h and 6h polymerization time duration of polydimethylsiloxane liquid precursors in corona discharges.

The GD-OES technique was also used for analyzing the surfaces obtained by ion implantation and deposition by immersion in a new plasma source. The processing plasma consists in applying a supplementary HV pulse under RF field so that the negative pulse applied on the target find a background plasma about 10 times denser than conventional low pressure plasma (10^{10} cm^{-3}) [21]. The metallic samples (copper and brass) implanted with nitrogen ions and non-metallic surfaces implanted with metal ions (copper) were analyzed depth profile GD-OES technique in order to assess the efficiency of the new plasma source.

The experimental setup for ion implantation based on the new method of plasma density enhancement, consists of a chamber divided in two volumes by a grounded grid (see Fig. 3) [21]. Capacitive coupled RF plasma was continuously and asymmetrically generated in the large part in nitrogen gas at low pressure (few Pa). High voltage (HV) pulsed discharges are periodically generated in the smallest part of the chamber.

The time resolved electric characteristics and plasma parameters are presented in and Fig. 4, where it can be seen that plasma density is periodically increased by an order of magnitude so that the synchronized negative pulses applied on the target for ion implantation find a background plasma about 10 times denser. This behavior can be attributed to a supplementary ionization process sustained by the energy accumulated in metastable atoms during the HV discharges [22].

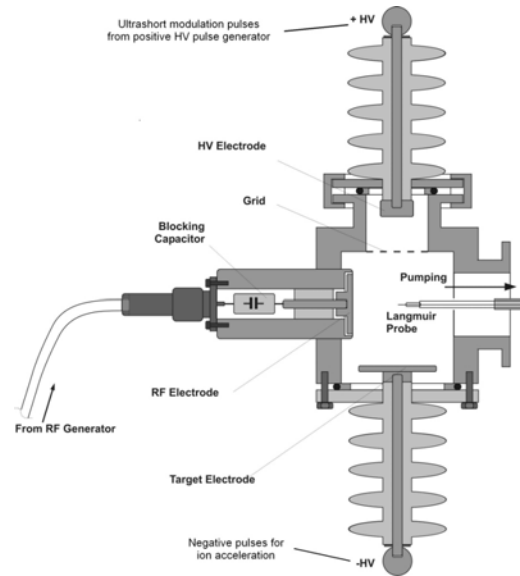


Fig. 3. Experimental Setup

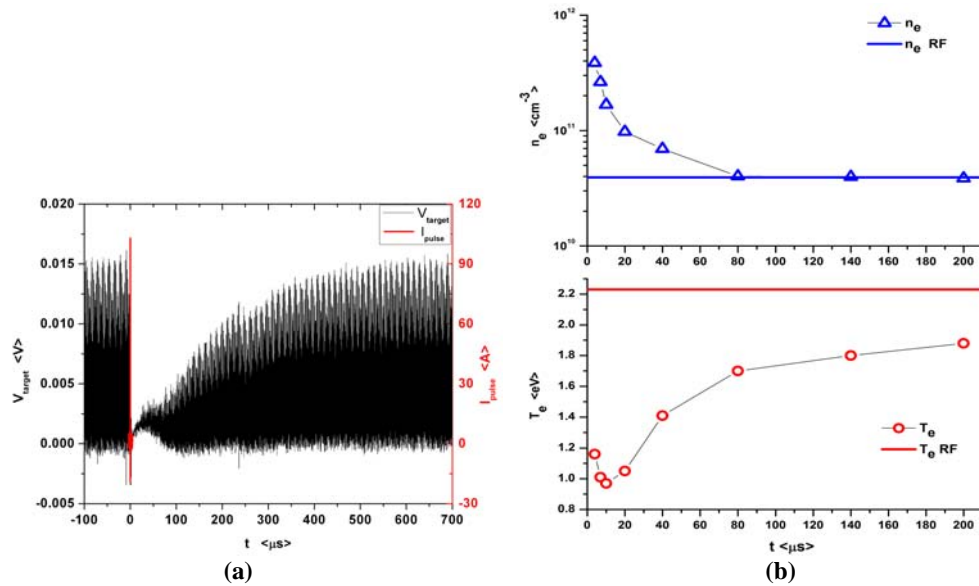


Fig. 4. a) RF voltage signal measured on the target electrode (V_{target}) and current signal (I_{pulse}) of positive pulsed discharge (in red); b) Time evolution of plasma parameters (plasma density, n_e and electron temperature, T_e)

Both, metallic and non-metallic processed surfaces were analyzed by GD-OES techniques. As it is well known, GD-OES is a destructive surface analysis

technique as craters of few millimeters in diameter and up to hundreds of microns in depth remain after the analyses. Examples of metallic surfaces with remaining craters can be observed in Fig. 5. a). Depth profiles of nitrogen implanted in copper and brass samples using the new plasma source operated in both, transient RF and classical RF discharges are presented in Fig. 5. b). The time (t) on the X axes is correlated with crater depth by sputtering rate. A calibration for various types of samples must be done.

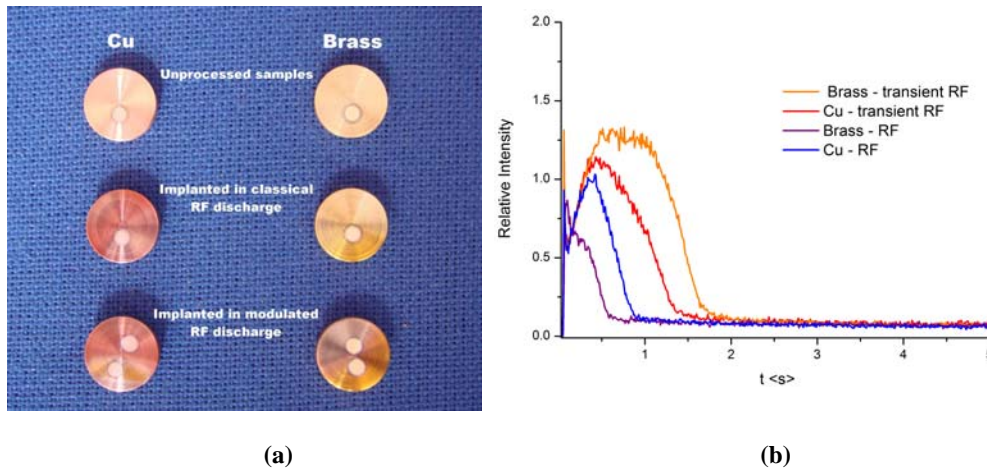


Fig. 5 a) Copper and brass samples processed by nitrogen ion implantation and analyzed by GD-OES method; b) GD-OES analysis: nitrogen depth profiles implanted in copper and brass samples using the new source operated in both, transient RF discharge and classical RF discharge.

Nevertheless, the GD-OES is a very powerful and versatile analytical diagnostic technique; it is based on emission spectroscopy, which has its limitations. On the other hand this technique implies sputtering processes which damage the analyzed surface. That is why to obtain important complementary information without destroying the analyzed surface, other methods like X-Ray Photoelectrons Spectroscopy (XPS) technique [23], or IR spectroscopy could be used.

3. Conclusions

Both, GD-OES and GD-TOFMS are very powerful and versatile analytical diagnostic techniques for investigation of different type of thin layers obtained by a large variety of plasma processing methods like, polymerization of PDMS liquid precursors in atmospheric pressure corona discharges or plasma immersion ion implantation (PIII).

Comparatively to other diagnostics techniques, like IR spectroscopy and SEM imaging, GD-OES and GD-TOFMS techniques are not nondestructive methods, but very important complementary information can be obtained from elemental depth profiles.

REFERENCES

- [1]. A. Surmeian, C. Diplasu, A. Groza, M. Ganciu, P. Belenguer, A. Tempez “Amplification of noble gas ion lines in the afterglow of a pulsed hollow cathode discharge and possible benefit for analytical glow discharge mass spectrometry”, *Analytical and Bioanalytical Chemistry*, **vol.388**, no.8, 2007, pp. 1625-1629
- [2]. A. Surmeian, C. Diplasu, A. Groza, R. Stoian, M. Ganciu, I. I. Popescu, “Absorption spectroscopy with intense pulsed calibrated source”, *Journal of Optoelectronics and Advanced Materials*, **vol.7**, no.4, 2005, pp. 2183-2188
- [3]. A. Surmeian, C. Diplasu, A. Groza, M. Ganciu, P. Chapon, I. I. Popescu, “An absorption spectroscopy technique for high voltage pulsed discharge afterglow plasma investigation”, *Optoelectronics and Advanced Materials-Rapid Communications*, **vol.4**, no.6, 2010, pp. 845-848
- [4]. A. Surmeian, C. Diplasu, A. Groza, M. Ganciu, “Ionization mechanism of sputtered atoms in analytical GDMS system operation”, *Romanian Reports in Physics*, **vol.60**, no.3, 2008, pp. 609-614
- [5]. A. Groza, A. Surmeian, C. Diplasu, D. Vinteler, M. Ganciu, “Modelling of the processes involved in the temporal evolution of the Ar metastable atoms density in the afterglow of high voltage pulsed discharges”, *Romanian Journal of Physics*, **vol.56**, Supplement S, 2011, pp. 83-89
- [6]. A. Surmeian, C. Diplasu, A. Groza, M. Ganciu, I. I. Popescu, “Ar II and Ar III kinetics in the afterglow of pulsed high current density hollow cathode discharge”, *Journal of Optoelectronics and Advanced Materials*, **vol.7**, no.5, 2005, pp. 2401-2404
- [7]. A. Surmeian, C. Diplasu, A. Groza, P. Chapon, A. Tempez, M. Ganciu, “Ionization and excitation processes in analytical plasma of GDOES and GDMS systems working in pulsed rf regime” *Romanian Journal of Physics*, **vol.56**, Supplement S, 2011, pp. 114-119
- [8]. A. Surmeian, A. Groza, C. Diplasu, C. Atanasiu, A. Popescu, D. Savastru “The gas temperature determination in the pulsed hollow cathode discharge”, *Romanian Reports in Physics*, **vol.65**, no.3, 2013, pp. 869-877
- [9]. A. Surmeian, A. Groza; C. Diplasu, M. Ganciu, C. M. Teodorescu, A. Tempez, P. Chapon, “Photonic molecular effects associated to the sputtering process in a glow discharge optical emission spectrometer”, *Optoelectronics and Advanced Materials-Rapid Communications*, **vol.3**, no.1, 2009, pp. 40-43
- [10]. A. Surmeian, C. Diplasu, A. Groza, M. Ganciu, I. I. Popescu, “A new ionization process in the afterglow of pulsed hollow cathode discharge *Journal of Optoelectronics and Advanced Materials*, **vol.8**, no.4, 2006, pp. 1414-1417
- [11]. A. Groza, A. Surmeian, C. Diplasu, C. Luculescu, P. Chapon, A. Tempez, M. Ganciu, “Physico-chemical processes occurring during polymerization of liquid polydimethylsiloxane films on metal substrates under atmospheric pressure air corona discharges”, *Surface and Coatings Technology*, **vol.212**, 2012, pp. 145-151
- [12]. A. Groza “Review of the processes identified during the polymerization of organic and organosilicon liquid films in atmospheric pressure air corona discharges”, *Romanian Reports in Physics*, **vol.64**, Supplement S, 2012, pp. 1227-1242

- [13]. A. Groza, A. Surmeian, C. Diplasu, M. Ganciu, P. Chapon, I. I. Popescu, "Spectral investigations of the processes observed at polydimethylsiloxane polymer-substrate interface during its polymerization process in negative and positive corona discharges Journal of Optoelectronics and Advanced Materials, **vol.12**, no.11, 2010, pp. 2311-2314
- [14]. A. Groza, A. Surmeian, C. Diplasu, M. Ganciu, "Evidence of nitrogen ions in organic and anorganic polymer layers generated in discharges at atmospheric pressure", Romanian Reports in Physics, **vol.60**, no.3, 2008, pp. 603-607
- [15]. C. L. Popa, A. Groza, P. Chapon, C. S. Ciobanu, R. V. Ghita, R. Trusca, M. Ganciu, D. Predoi, "Physicochemical analysis of the polydimethylsiloxane interlayer influence on a hydroxyapatite doped with silver coating" Journal of Nanomaterials, **vol.2015** Article ID 250617, 2015, 10 pages
- [16]. A. Groza, A. Surmeian, M. Ganciu, I. I. Popescu, "Infrared spectral investigation of the linseed oil polymerization in a corona discharge in air at atmospheric pressure", Europhysics Letters, **vol.68**, no.5, 2004, pp. 652-657
- [17]. A. Groza, M. Ganciu-Petcu, A. Surmeian, I. I. Popescu, "Oils polymerization induced by corona discharges at atmospheric pressure", Molecular Crystals and Liquid Crystals, **vol.416**, 2004, pp. 217-222
- [18]. A. Groza, A. Surmeian, M. Ganciu, I. I. Popescu, "Infrared spectral investigation of organosilicon compounds under corona charge injection in air at atmospheric pressure", Journal of Optoelectronics and Advanced Materials, **vol.7**, no.5, 2005, pp. 2545-2548
- [19]. A. Groza, A. Surmeian, M. Ganciu, R. Medianu, I. I. Popescu, "SiO₂ - Like thin films generation in corona discharges in air at atmospheric pressure: IR spectroscopy and atomic force microscopy investigations", Journal of Optoelectronics and Advanced Materials, **vol.7**, no.4, 2005, pp. 2159-2164
- [20]. A. Groza, A. Surmeian, C. Diplasu, C. Luculescu, C. Negrila, M. Ganciu, "Generation of porous alumina layers in a polydimethylsiloxane/hydrogen peroxide medium on aluminum substrate in corona discharges", Journal of Nanomaterials, **vol.2014**, Article ID 578720, 2014, 6 pages
- [21]. C. Diplasu, A. Surmeian, A. Groza, M. Ganciu, "Synchronous plasma enhancement in RF-driven plasma source for ion implantation", Surface and Coatings Technology, **vol.203**, no.19, 2009, pp. 2858-2862
- [22]. C. Diplasu, A. Surmeian, H. Fujita, "Ionizing role played by atomic metastable species in rf plasma modulated by short high current pulsed discharges", Journal of Optoelectronics and Advanced Materials, **vol.7**, 2005, p. 2397- 2400
- [23]. C. Diplasu, "Enhanced implantation and deposition of metal ions by immersion in synchronous modulated RF -driven plasma" Romanian Reports in Physics, **vol.66**, 2014, pp. 737-745.