

## **ION ACCELERATION ENHANCEMENT IN LASER-GENERATED PLASMAS BY METALLIC DOPED HYDROGENATED POLYMERS**

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**ABSTRACT.** Laser-generated plasmas in vacuum were obtained by ablating hydrogenated polymers at the Physics Department of the University of Messina and at the PALS Laboratory in Prague. In the first case a 3 ns, 532 nm Nd:Yag laser, at  $10^{10}$  W/cm<sup>2</sup> intensity was employed. In the second case a 300 ps, 438 nm iodine laser, at  $5 \times 10^{14}$  W/cm<sup>2</sup> intensity was employed. Different ion collectors were used in a time-of-flight configuration to monitor the ejected ions from the plasma at different angles with respect to the direction normal to the target surface. Measurements demonstrated that the mean ion velocity, directed orthogonally to the target surface, increases for ablation of polymers doped with metallic elements with respect to the nondoped one. The possible mechanism explaining the results can be found in the different electron density of the plasma, due to the higher number of electrons coming from the doping elements. This charge enhancement increases the equivalent ion voltage acceleration, i.e. the electric field generated in the non-equilibrium plasma placed in front of the ablated target surface.

### **1. Introduction**

The characterization of laser-generated plasmas follows different analytical techniques, such as optical spectroscopy, mass spectrometry, Langmuir probes, ion and electron energy analyzers, etc.. A particular attention is devoted to simple ion collectors (IC) used in time-of-flight configuration which permit to detect ions and electrons and the laser photo-peak signal coming from the photoelectric effect induced by laser and plasma photons. Such collectors permit to measure the mean ion velocity and kinetic energy, when the target-collector distance is known [1]. Sometimes, using long distances or external magnetic or electric fields, IC permits to separate the different ion charge states and to measure, separately, the kinetic energy of the ions vs. their charge state [2].

Thermal interactions, adiabatic thermal expansion in vacuum and Coulomb interactions are at the basis of the mechanisms of ion acceleration in laser-generated plasma processes. Measurements of ion energy distributions, performed with electrostatic ion energy analyzers, permitted to show that the distribution follows a Coulomb-Boltzmann-Shifted (CBS) function, indicating that an equivalent plasma temperature is responsible of the thermal velocity and of the plasma expansion velocity of ions gas in vacuum; this last velocity occurs

mainly along the normal to the target surface. Increasing the charge state the distributions are shifted towards higher energies, as a result of the ion acceleration due to an equivalent voltage generated in the non-equilibrium charge distribution and applied mainly along the target normal direction [3].

The electron density of the plasma influences strongly the plasma properties, such as the temperature, the mean ion energy, the charge state distribution, the fractional ionization, the Debye length and the angular distribution of ions and electrons emitted from the plasma.

The plasma obtained irradiating hydrogenated polymers contains mainly carbon and hydrogen ions, which have higher velocity. Also  $C_xH_y$  ion groups, carbon clusters and elements coming from adsorbed gases and contaminants can be produced. The plasma electron density, in these cases, is lower with respect to that one coming from metal irradiation, which permits to introduce an higher number of electrons in the plasma gas, specially if heavy elements are ablated. In this work the differences between laser-generated plasmas from pure hydrogenated polymers and metal doped polymers, obtained introducing a known amount of metal component in the polymeric target, are investigated. The study concerns overall the comparison from the point of view of the different kinetic energies and angular distributions of the ions emitted from the plasma.

## 2. Experimental section

The lasers employed for this experiment were the Nd:Yag laser of the Physics Department of Messina University and the iodine laser of PALS (Prague Asterix Laser System) in Prague. The first operates at 532 nm wavelength, 3 ns pulse duration and 200 mJ maximum pulse energy, whereas the second operates at the third harmonic, 438 nm, with a pulse duration of 400 ps and a maximum used laser pulse of 120 J. In both cases the laser beam was focused on the planar surface of the polymeric target placed in the vacuum chamber, at  $10^{-6}$  mbar pressure, to obtain an intensity of  $10^{10}$  W/cm<sup>2</sup> for the Nd:Yag and  $10^{15}$  W/cm<sup>2</sup> for the PALS laser. Lasers operated in single shots irradiation and 30° incident angle with respect to the target normal direction.

For the experiment developed in Messina laboratory, two kinds of polymeric targets were prepared; the first one was polyethylene (PE) target, 2 cm x 2 cm and 1mm thick, pure and doped with 1-10 % in weight of platinum; the second one was pure mylar film with 100  $\mu$ m in thickness, and a mylar film covered by a thin layer (50 nm thickness) of gold. In this experiment only one IC ion detector was used, placed at 0° angle and at 76,5 cm distance from the target.

For the experiment performed at PALS laboratory the polymeric targets were prepared as a thin film, 20  $\mu$ m in thickness, mounted on an Al backing surface placed at 2 mm distance from the thin polymeric film. Polyethylene (PE,  $-CH_2-$  monomer), Poly-vinyl alcohol (PVA,  $-C_2H_4O-$  monomer) and Polyvinylacetate (OCT,  $-C_4H_6O-$  monomer) were used as targets. Such polymers have a similar H/C ratio, ranging between 1.5 (OCT) to 2 (PVA and PE). They were prepared by solution of liquid polymer and a known amount of very thin grain sized doping (Br, Cu, and Au). The doping content was maintained from 2 % to 10 % weight. The polymer was doped uniformly in its bulk. In order to measure the average ion energy and the angular distributions of the current density of emitted ions, four ion collectors (ICs) were placed inside the vacuum chamber, at the following angles:

$0^\circ$  (IC1);  $25^\circ$  (IC2);  $33^\circ$  (IC3) and  $41^\circ$  (IC4), with respect to the target normal direction and at 60 cm distance from the target surface, with a collection area of  $0.13 \text{ cm}^2$  for each one. Fig. 1 shows the experimental set-up scheme employed at the Physics Department of Messina University (a) and at PALS laboratory (b).

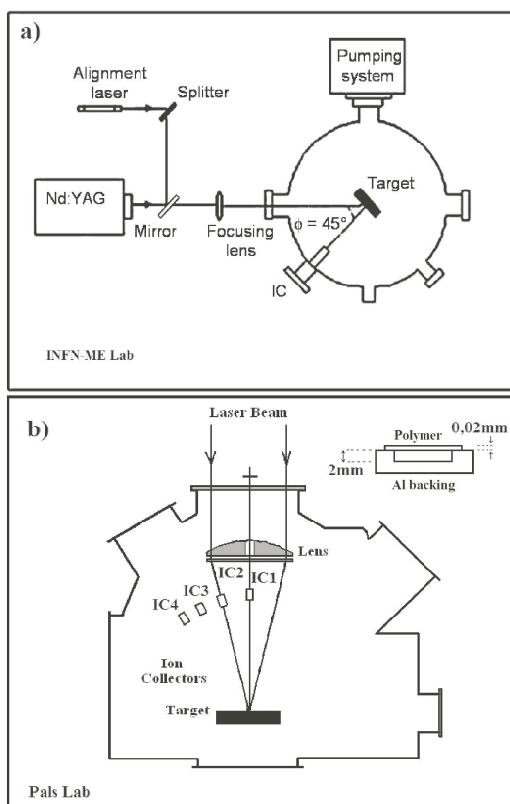


FIGURE 1. Experimental set-up scheme employed at the Physics Department of Messina University (a) and at PALS laboratory (b).

The ICs, delivering charge-integrated and time-resolved ion current signals, give information about the ion emission yield, the ion velocity and the angular distribution of the ions emitted from the plasma. The ion velocities were measured by time-of-flight (TOF) technique and by recording the ion spectra on a fast storage oscilloscope. Spectra show the laser photo-peak (start signal) and the ion large peak (stop signal) through which it was possible to evaluate the mean emitted ion energies. A simple formula used for the ion velocity distribution was derived for one-dimensional experimental configuration [4]:

$$\left| \frac{dN}{dv} \right| = \frac{dN}{dt} \left| \frac{dt}{dv} \right| = \frac{j_{IC}}{eq} \left| \frac{dt}{dv} \right| \frac{t^2}{eqmRL} U(t) \quad (1)$$

where  $dN/dv$  is the ion velocity distribution,  $dN/dt$  is the ion distribution vs. time,  $L$  is the ion flight length (target-IC distance),  $j_{IC}$  is the measured IC-ion current,  $e$  is the elementary charge,  $q$  is the charge-state of ions,  $t$  is the TOF time,  $U$  is the voltage measured by an oscilloscope with the circuit load  $R$  and  $m$  is the ion mass.

Experimental data were elaborated by converting the TOF spectra in velocity spectra, as described by eq. (1), and by assuming that the ion velocity distribution follows a Coulomb-Boltzmann-Shifted (CBS) function

$$F(v) = A \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^3 \exp \left[ - \left( \frac{m}{2k_B T} \right) (v - v_k - v_c^2) \right] \quad (2)$$

where  $A$  is a normalization constant,  $m$  is the ion mass,  $k_B$  is the Boltzmann constant,  $T$  is the plasma temperature,  $v$  is the total velocity along the normal direction to the target surface,  $v_k$  is the adiabatic plasma expansion velocity and  $v_c$  is the Coulomb velocity [5].

### 3. Results

**3.1. Low-energy laser ablation.** Preliminary experiments were performed at low laser intensity with the aim to observe differences between the electric field developed inside the plasma produced by laser ablation of pure polymers or metal doped/covered polymers. Fig. 2a and 2b shows a comparison between the IC spectra obtained at Messina Laboratory, converted into velocity distribution (open dots), for the ions detected ablating undoped polyethylene (a) and 2 % platinum doped polyethylene (b) using a 150 mJ laser pulse energy irradiation. The insets of the two spectra show the corresponding detected TOF-IC signals. The comparison shows a peaks shift towards higher velocity in the case of metallic doped polymer ablation. The fit of the experimental data (full line) was obtained using a CBS function. The deconvolution process indicates that the spectra contains an amount of fast  $H^+$  ions, with a mean velocity of about  $1.6 \times 10^5$  m/s and  $1.75 \times 10^5$  m/s coming from pure and from doped PE, respectively. Moreover, three carbon charge states can be observed, with kinetic energy of 260 eV, 503 eV and 752 eV for  $C^{1+}$ ,  $C^{2+}$  and  $C^{3+}$  respectively, and an energy shift of about 246 eV between them, for the case of undoped polyethylene. The energies increase to 290 eV, 633 eV and 986 eV for the three charge states, respectively, with an energy shift of about 348 eV, for the case of doped polymer. In both cases, the best CBS distribution fits were obtained assuming a plasma temperature of 2.5 eV.

Similar results, indicating that the ion velocity increases in metallic doped polymers, were obtained for mylar covered by a thin Au film. Fig. 2c and 2d shows a comparison between the IC spectra, after velocity conversion, obtained at Messina laboratory for the ions detected ablating undoped mylar films (c) and 50 nm Au thickness covered mylar films (d), using 150 mJ laser energy irradiation. The insets of the two spectra show the corresponding detected TOF-IC signals. Also in this case the comparison shows an evidence of the carbon ion peaks shift, produced by the mylar, towards higher velocity in the case of metallic mylar coverage. The CBS deconvolution process indicated that the spectrum contains three carbon charge states with kinetic energy of 246 eV, 650 eV and 1050 eV for  $C^{1+}$ ,  $C^{2+}$  and  $C^{3+}$ , respectively, in the case of pure mylar, with a regular energy shift of 400 eV between them. The energies increase to 322 eV, 850 eV and 1398 eV for the three charge states, respectively, with an energy shift of 538 eV, in the case of mylar-gold

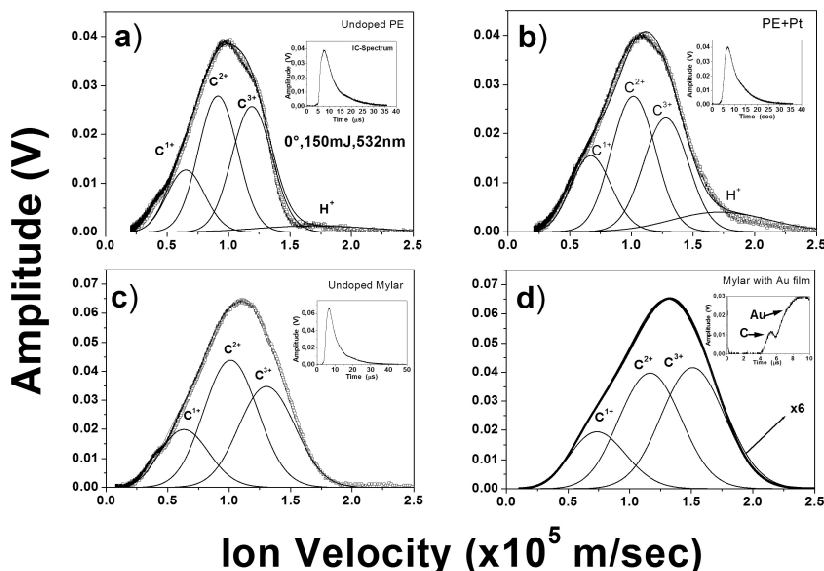


FIGURE 2. Comparison between the TOF-IC spectra (insert) and experimental ion velocity distribution (open points), obtained at Messina Laboratory, for the ions detected ablating undoped polyethylene (a), 2 % platinum doped polyethylene (b), undoped mylar film (c) and 50 nm Au covered mylar film (b). All spectra show the deconvolution components (continuous lines) due to different ions and charge state.

covered polymer. The best CBS distribution fits were obtained assuming a plasma temperature of 4.4 eV and 5.6 eV for the spectrum with pure mylar and mylar-gold covered, respectively.

Thus the measurements performed at low laser intensities demonstrated that the ion acceleration in the laser-generated plasma increases of about 100 eV for polymers containing metallic traces, such as doping or as thin covered films. This result is probably due to the increment of the electron density of the plasma due to the electrons injected from the metal doping or coverage. This density increase, in facts, produces a plasma temperature increase and a Coulomb interaction increase and consequently an higher plasma ion acceleration.

**3.2. High-energy laser ablation.** Experiments of laser ablation with high pulse energy have been performed on different polymeric targets. The four insets of the four spectra of Fig. 3 shows the TOF-IC signals relative to the irradiation, at 120 J laser pulse energy, incidence angle of  $0^\circ$  (IC placed along the normal to the target surface), of pure PE (a), polyethylene doped with 3 % Br (b), OCT doped with 2 % Cu (c) and PVA doped with 10 % Au (d). Such comparison indicates that generally the shape of TOF ion spectrum is similar for the four cases, although a different ion yield can be detected due to the different polymeric nature. Generally the ion spectra contain signals due to H, C and O ions, to  $C_xH_yO_z$  ionized species and to traces of metallic doping.

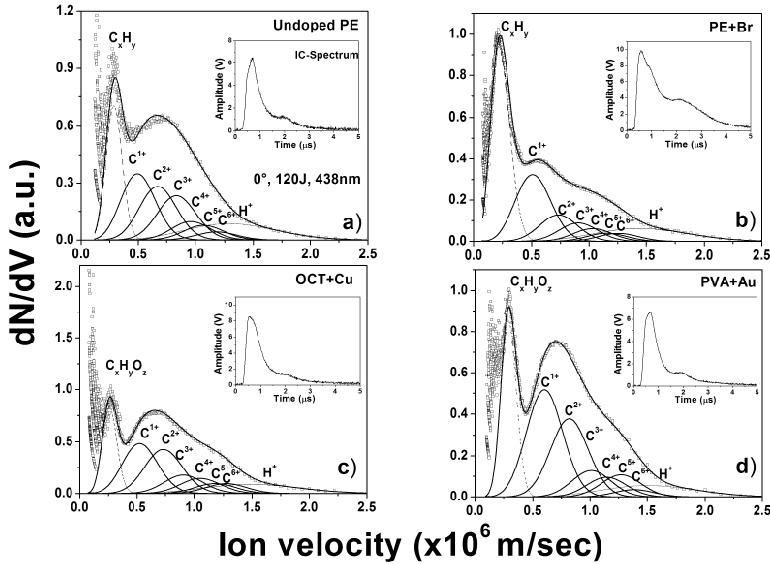


FIGURE 3. Experimental ion velocity distribution (open points) and deconvolution peaks (continuous lines) obtained at PALS laboratory for ablation of pure polyethylene (a), polyethylene doped with 2% Br (b), OCT doped with 2% Cu (c), and PVA doped with 10% Au (d). Inserts in figures show the TOF-IC spectra.

Converting the TOF spectra in ion velocity spectra, as described by eq. (1), the comparison between the IC spectra in pure and doped polymer appears so as reported in Fig. 3a, 3b, 3c and 3d. In this case the spectra are more complex because the carbon atoms can be full ionized and ion components from  $C^{1+}$  up to  $C^{6+}$  are detected, in agreement with previous our measurements [6]. The TOF-IC spectra, obtained along the normal to the target surface, converted in ion velocity distributions (open dots) can be deconvolved in the different ion charge state contributions. The deconvolved peaks reported inside each spectrum have been obtained assuming that their shape follows a Coulomb-Boltzmann-shifted function. Our attention was devoted mainly to the measurement of the hydrogen and carbon ion components vs. their charge state. The deconvolution contributes to the total IC ion yield show a significant velocity shift depending on the ion specie and charge state. According to this data approach the hydrogen ion is found to be the faster specie, with a velocity going from  $1.55 \times 10^6$  m/s for pure PE to  $1.64 \times 10^6$  m/s for Br-doped PE. Carbon ions have a velocity increasing with the charge state, going from  $4.9 \times 10^5$  m/s for  $C^{1+}$  to  $1.2 \times 10^6$  m/s for  $C^{6+}$  for pure PE and going from  $5.1 \times 10^5$  m/s for  $C^{1+}$  to  $1.3 \times 10^6$  m/s for  $C^{6+}$  for Br-doped PE. The deconvolution process obtained using eq. (2) indicates that the equivalent ion plasma temperature is about 250 eV in both cases, i.e. for doped and no-doped PE irradiation presented in Fig. 3a and 3b.

Fig. 3c and 3d show the experimental ion velocity distributions (open dots) directed towards the normal to the target surface for OCT-Cu doped and PVA-Au doped respectively. The deconvolution peaks reported in the spectra of Fig. 3c and 3d are due to the detection of hydrogen, carbon and oxygen ions with different energy and charge state. The deconvolution process demonstrates that the mean velocity of the faster particles (protons) is  $1.86 \times 10^6$  m/s and  $1.65 \times 10^6$  m/s for PVA-Au doped and for OCT-Cu doped, respectively. The proton velocity increment, due to the metal doping of the polymer, is 20 % and 6.5 % in the two cases, respectively. The oxygen amount with respect to the carbon one, is about 50 % and 25 % for PVA and OCT, respectively, so the oxygen contribution to the deconvolution of the TOF signal is much more low than carbon one. Moreover, the greater mass of oxygen moves its contribution towards the lower velocity signal. In PVA and OCT the  $O^{8+}$  deconvolution peak is superimposed to  $C^{6+}$  peak but the oxygen contribution is low due to the higher ionization potential and to its lower concentration. In conclusion, as a first approximation, PVA deconvolution peaks are due also to a significant oxygen contribution, of the order of some tens percents, while OCT deconvolution peaks are due mainly to carbon because only a little contribution of oxygen is here present.

C-ions have a velocity increasing with the charge state, going from about  $6 \times 10^5$  m/s for  $C^{1+}$  to  $1.46 \times 10^6$  m/s for  $C^{6+}$  for PVA-Au doped, while for the irradiation of Cu-doped OCT the measurements give a mean velocity of about  $5.2 \times 10^5$  m/s for  $C^{1+}$  and of about  $1.32 \times 10^6$  m/s for  $C^{6+}$ . The weightier groups ( $C_xH_yO_z$ ) are slower and generally their velocity is of the order of  $3 \times 10^5$  m/s or less. Thus, also in this case experimental data demonstrated that the ion velocity along the normal direction increases when the polymer contains metallic atoms. However, this increment generally remains below 20% for the used doping species and concentrations and for the used laser irradiation geometries.

Also for the spectra reported in Fig. 3c and 3d the eq. (2) function, used to fit the velocity distributions of each ion specie, indicates that the plasma equivalent temperature is 250 eV and that a regular velocity increment is found with the charge state. For example at  $0^\circ$  angle (normal direction) a value of velocity increment of  $4.8 \times 10^5$  m/s per charge state and of  $5.22 \times 10^5$  m/s per charge state is found for C-ions produced irradiating pure polyethylene and Br-doped polyethylene films, respectively.

The validity of the performed fits is confirmed also by the relative amount of the ion yields with their charge states. The ion yields, in facts, decreases exponentially with the charge state, in agreement with the fast increment of the ionization potentials of the element. Fig. 4 reports the carbon ion yield contribution, obtained by the yield of the deconvolution peaks, vs. the ion charge state, for the experiments at low laser energy (a) and at high laser energy (b). Data are in agreement with the law of exponential decay of the ionization potential increment of carbon atoms with its charge state given by Lotz theory [7].

The IC spectra shapes and ion yields change significantly with the detection angle with respect to the target normal direction. As an example, Fig. 5 compares results obtained detecting ions from Br doped PE, at  $0^\circ$ ,  $25^\circ$ ,  $33^\circ$  and  $41^\circ$  detection angle, maintaining the same target-collector distance. All deconvolution distributions of Fig. 5 indicate an equivalent plasma temperature of 250 eV. The hydrogen mean energy is 14 keV at  $0^\circ$  and about 9 keV at  $41^\circ$ . The  $C^{1+}$  mean energy is 16.5 keV and 9.7 keV at  $0^\circ$  and  $41^\circ$ , respectively. The  $C^{6+}$  mean energy is 103 keV and 59.7 keV at  $0^\circ$  and  $41^\circ$ , respectively.

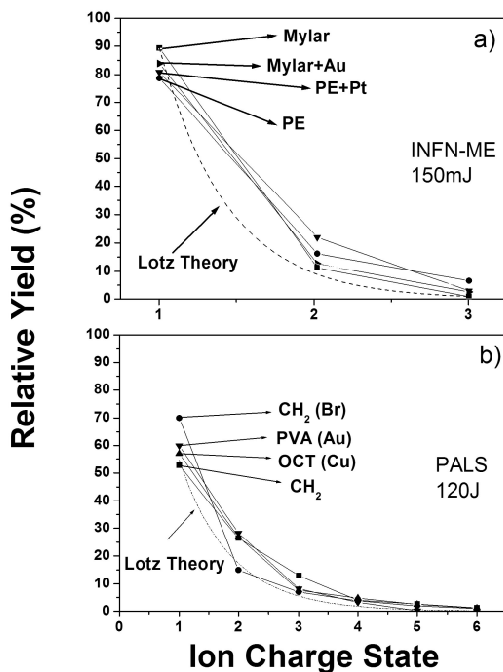


FIGURE 4. Carbon relative ion yield vs. ion charge state (full points) and comparison with Lotz theory (dashed line), at low laser energy (a) and high laser energy (b).

By increasing the detection angle, the ion yield decreases and the peak of the velocity distribution decreases also, indicating that the ion emission from plasma is cantered along the normal to the target direction and that the ion acceleration is maximum along such direction, in agreement with previous measurements of ion angular distributions [3].

In terms of kinetic ion energy a stronger energy gradient is found at  $0^\circ$  while a negligible gradient is found at angles higher than  $25^\circ$ . The energy shift for single ionized species ranges between 14 keV, for the pure polymers, and 22 keV, for the Au-doped polymer. As an example, the ion energy shift measured for the pure PE and doped polymers vs. concentration of doping atoms and for different charge state is reported in Fig. 6a. This plot shows that the  $C^{1+}$  energy shift at  $0^\circ$  in the pure PE is 14 keV and that this value increases significantly up to 22 keV for Au-doping, while it is negligible for Br and Cu doped polymers. Moreover, the increment disappears at angles higher than  $25^\circ$ . The energy shift increment is more evident for the  $C^{6+}$  due to the Coulombian ion acceleration.

On the basis of the obtained results an equivalent ion acceleration voltage can be calculated for the non-equilibrium plasma produced ablating different kind of polymers. The plot of Fig. 6b shows the equivalent acceleration voltage vs. concentration of doping atoms, obtained at different detection angles for the hydrogenated polymers doped with Br, Cu and Au. At  $0^\circ$  detection angle, from 14 kV ion acceleration measured in the as



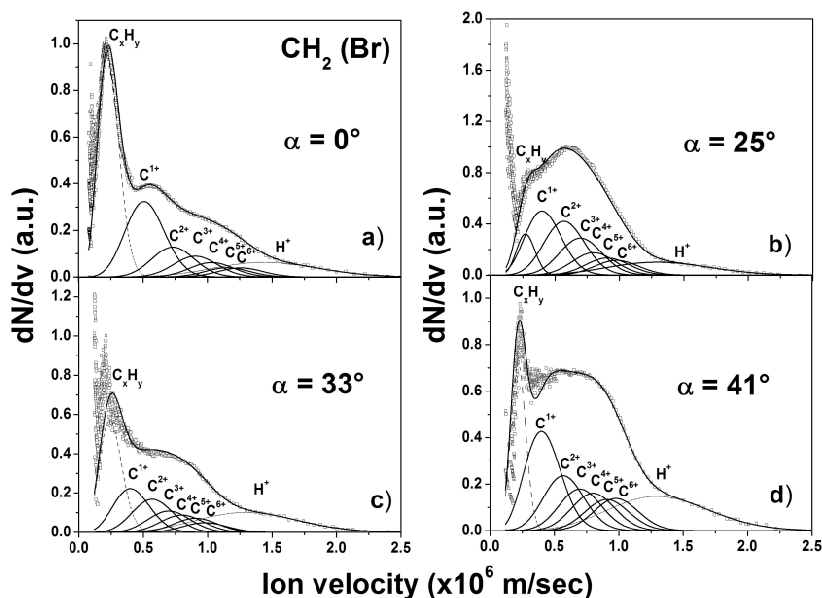


FIGURE 5. Comparison of results obtained at PALS laboratory detecting ions from PE doped with 2% Br at  $0^\circ$  (a),  $25^\circ$  (b),  $33^\circ$  (c), and  $41^\circ$  (d) detection angle and 60 cm target-collector distance.

prepared PE the equivalent voltage increases up to 22 kV for the Au doped-OCT polymer, indicating that an evident enhancement of the ion acceleration occurs in the case of doping with heavy metallic elements, i.e. of elements with high electron densities.

#### 4. Discussion and conclusions

The present work gives some special information about the ion acceleration mechanisms produced in laser-generated plasma. Due to the non-equilibrium spatial distribution of the electrical charges in the ionized gas, produced by the faster electron emission and by the slower ion emission, acceleration voltages can be developed along the expansion direction. Although the ion acceleration is relatively high for ablation of thin polymers, the metal-doped polymers show clearly an enhancement of the ion acceleration process. This interesting result can be due to the introduction in the plasma of a great number of electrons supplied by the element doping [8]. The laser ablation of doped polymers, in fact, increases the electron density of the plasma and consequently the value of the ion acceleration voltage, which is generated by the positive charge of the target, which lost fast electrons, and the negative electron cloud, quickly emitted from the target, in the first initial instants of the laser ablation process, according to a model previously described [9].

The data analysis is performed with TOF ion spectra deconvolution approach by using the Coulomb-Boltzmann-shifted function presented in previous articles [5]. TOF spectra recovered a number of hidden peaks, which makes a more detailed classification of the

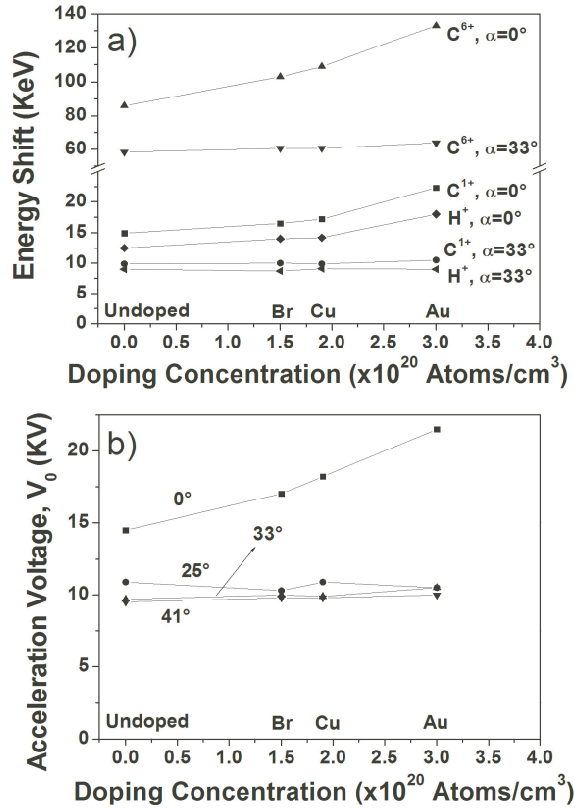


FIGURE 6. Ion energy shift measured at PALS laboratory for single and six times ionized carbon atoms vs. doping concentration atoms, for  $0^\circ$  and  $33^\circ$  detection angles (a) and equivalent acceleration voltage vs. doping concentration atoms at different detection angles.

different ion groups. The recovered peaks give more detailed information on the single ion specie, energy and charge state. The TOF-IC spectra deconvolution gives an exact determination of the peak velocity and energy and improve the analysis of the reconstructed ion yields and charge states. The angular distribution of emitted ions shows that the emission is not isotropic and that the maximum emission is placed along the normal to the target surface, in agreement with previous measurements [3]. However, the width of the angular distributions obtained in these investigations is higher with respect to similar experiment obtained irradiating thick polymeric films. Work is in progress to investigate about the influence of the target geometry, the influence of higher doping content in the polymer and the ion angular distribution of ejected particles.

## Acknowledgements

Authors thank Prof. J. Wolowski, Dr. J. Badziak, Dr. P. Parys, Dr. M. Rosinski of the Institut of Plasma Physics and Laser Microfusion (IPPLM) of Warsaw (Poland), Dr. L. Laska, Dr. J. Krasa, Dr. J. Ullschmied, Dr. E. Krousky, Dr. K. Masek, Dr. M. Pfeifer of the Academy of Science of Czech Republic (ASCR) and PALS Laboratory of Prague (Czech Republic) and Dr. L. Dareshwar of the Bhabha Atomic Research Centre (BARC), Trombay, Mumbai (India) for the deep collaboration activities devoted to develop experiments using high energy laser-generating plasmas ablating polymer materials.

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Presented: 14 May 2008; published online: 4 May 2009.

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