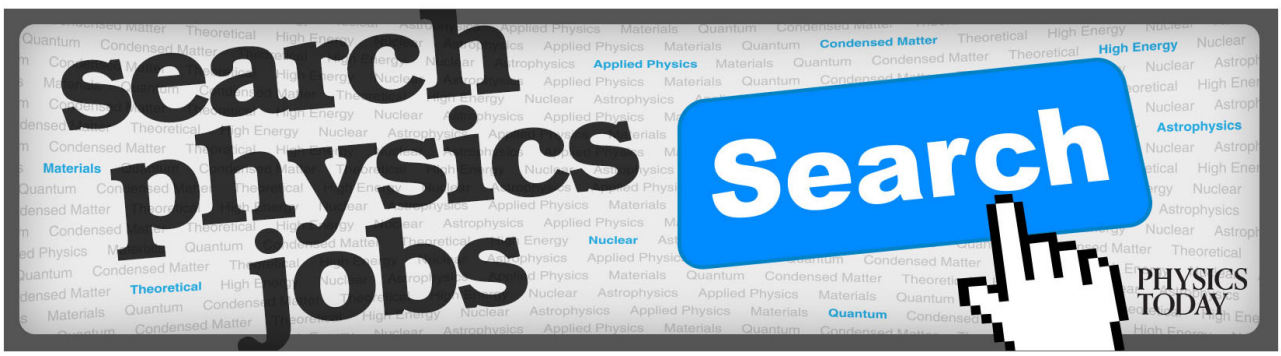
AIP | Review of Scientific Instruments

New method of plasma immersion ion implantation and also deposition of industrial components using tubular fixture and plasma generated inside the tube by high voltage pulses

Mario Ueda, Ataide Ribeiro da Silva, Elver J. D. M. Pillaca, Samantha F. M. Mariano, Rogério de Moraes Oliveira, José Osvaldo Rossi, Carlos Mauricio Lepienski, and Luc Pichon

Citation: Review of Scientific Instruments **87**, 013902 (2016); doi: 10.1063/1.4939013
View online: http://dx.doi.org/10.1063/1.4939013
View Table of Contents: http://scitation.aip.org/content/aip/journal/rsi/87/1?ver=pdfcov
Published by the AIP Publishing



REVIEW OF SCIENTIFIC INSTRUMENTS **87**, 013902 (2016)

New method of plasma immersion ion implantation and also deposition of industrial components using tubular fixture and plasma generated inside the tube by high voltage pulses

Mario Ueda,[1,a)] Ataide Ribeiro da Silva,[1,2] Elver J. D. M. Pillaca,[1] Samantha F. M. Mariano,[1,2] Rogério de Moraes Oliveira,[1] José Osvaldo Rossi,[1] Carlos Mauricio Lepienski,[3] and Luc Pichon[4]

[1]*Associated Laboratory of Plasma, National Institute for Space Research, São José dos Campos, SP 12227-010, Brazil*

[2]*Associated Laboratory of Sensors and Materials, National Institute for Space Research, São José dos Campos, SP 12227-010, Brazil*

[3]*Department of Physics, Federal University of Paraná, Curitiba, PR 81531990, Brazil*

[4]*Institut Pprime -UPR 3346 CNRS-Université de Poitiers-ENSMA, Poitiers 86073, France*

(Received 18 June 2015; accepted 12 December 2015; published online 8 January 2016)

A new method of Plasma Immersion Ion Implantation (PIII) and deposition (PIII and D) for treating industrial components in the batch mode has been developed. A metal tubular fixture is used to allocate the components inside, around, and along the tube, exposing only the parts of each component that are to be ion implanted to the plasma. Hollow cathode-like plasma is generated only inside the tube filled with the desired gas, by applying high negative voltage pulses to the hollow cylindrical fixture which is insulated from the vacuum chamber walls. This is a very convenient method of batch processing of industrial parts by ion implantation, in which a large number of small to medium sized components can be treated by PIII and PIII and D, very quickly, efficiently, and also at low cost. © *2016 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4939013]

I. INTRODUCTION

Plasma immersion ion implantation (PIII)[1] is a method used for surface treatment of materials which is quite well known nowadays, especially by the researchers seeking the improvements of surface physical and chemical properties of industrial components by ion implantation.[2] Although its widespread use in industries has not been achieved yet, for applications that require high qualification, reproducibility and specific needs as in space engineering[3] and medical sciences,[4] PIII is meeting good acceptability due to its unique characteristics (possibility of three dimensional ion implantation).

Relatively high capital cost and not so simple operation of the ion implanter are some of the reasons why PIII has not yet been so popular in small plasma laboratories or industries worldwide compared to other settled surface treatments. In the case of nitrogen implantation, it competes with a more traditional plasma nitriding process that allows treatments of many metal components in the batch mode, at high temperatures (typically 600-700 °C), which result in thick (more than 100 μm), nitrogen rich layers, enhancing considerably the components' performance.[5] For hard coatings that could be carried out also by PIII, as DLC coatings, for example, other methods like CVD or PECVD are preferred and dominate the market, due to their lower cost, intense developments, and high efficiency.[6]

Meanwhile, ion implantation by the beam method is the mostly used one for moderate to high energy applications, as in the semiconductor field. For a more recent task of developing extremely small chips which demand very low energy implantations, PIII seems to meet the requirements and is starting to be employed in modern IT (Information Technology) related industries.[7]

Recently, the important and realistic industrial application of DLC internal coatings in large radius (half meter) and long pipelines (30 m) for petroleum extraction from pre-salt basins, using the PIII and D method has been demonstrated by Wei.[8] The internal coating of pipes has been the subject of research for some years[9] because of its high potential for many industrial applications. Chemical, food, pharmaceutical, ethanol, and other biofuels, as well as petroleum industries, are seeking advanced coatings for their tubes with different radial and length sizes. In the other limit, PIII and D was also successfully tested in the case of very small bore pipes (millimeter radius, half meter long), when internal coatings with DLC were obtained.[10]

So, other niche applications of PIII and PIII and D (deposition) which are more favorable for these methods of surface modification compared to other more traditional ones are being sought intensely while other few successful cases in aerospace, medical, and IT, as well as petroleum applications, as cited above, are being pursued strongly.

Plasmas are the source of ions in the PIII and PIII and D schemes. So, different methods of plasma production have been adapted for PIII and PIII and D processings. Glow discharge with controlled plasma potential,[11] RF,[12] microwave,[13] and arc plasma,[14] as well as plasma produced by high voltage glow discharge,[1] have been used in many PIII and PIII and D experiments. In some industrial applications, moderate to high temperatures are required during PIII, to

a)Email: ueda@plasma.inpe.br

enhance diffusion and attain thick treated layers. Very thick layers, rich in nitrogen, have been obtained by special PIII schemes, either by heated supports[15] or PIII inside a furnace, with a quartz vacuum chamber.[16] Auxiliary heating using the electrons from the plasma has allowed to surpass very high temperatures, as high as 1500 °C, while performing PIII of nitrogen in small samples of refractory materials as molybdenum and achieving very thick treated layers (>tens of μm).[17] On the other hand, PIII using the magnetic field with magnetic bottle configuration was tested successfully.[18,19] In particular, PIII with the magnetic field for the treatment of the internal parts of tubes of medium size radius (2–5.5 cm) and length (15–20 cm) with nitrogen implantation was demonstrated recently.[20]

So, by combining these two ideas, (1) metal tubular geometry fixture and (2) high density hollow cathode-like plasmas produced inside a tube by negative high voltage pulses, either with or without magnetic fields, we were able to develop PIII and PIII and D configurations that are very effective for the simultaneous ion implantation of many industrial workpieces in the batch mode, for the surface finishing of industrial components in the final form.

II. EXPERIMENTAL METHODS AND APPARATUS

The present experiment was performed using the PIII system depicted in Figure 1. The high voltage pulser is driven by a pulse power supply made by LIITS company (with a nominal maximum voltage and primary current of 1.5 kV and 250 A, respectively), shown in the left side of the figure. Then, for a typical pulser set-up of 50 μs and 1 kHz, we have $P = V \times I \times df$, with $df = 50 \times 10^{-3}$. Hence, $P = 375\,000 \times 50 \times 10^{-3} = 18.8$ kW. Including the efficiencies of the parts and operating it in the safe limits, 10 kW output is achieved which is satisfactory for us for the moment. This LIITS power supply is connected to the high voltage pulse transformer provided by STANGENES to deliver maximum outputs of 25 kV/20 A. Hence, in a typical PIII operation, $P1 = 10\,\text{kV} \times 5\,\text{A} \times df1 = 50 \times 10^3 \times 50 \times 10^{-3} = 2500\,\text{W}$ or 2.5 kW. It is a current controlled pulser and it is difficult to double the power (5 kW) without reaching the pulser component limits (heating and voltage and current limits of the components), so far. The maximum pulse length set up from the pulser manufacturer is 50 μs, with a minimum of 10 μs. However, the longer pulse set up leads to about 70 μs duration seen in the oscilloscope. As a function of the voltage, the longer the pulse, the lower the peak voltage achieved. For shorter pulses, higher voltages can be attained. Concerning the frequency, we observe the same effect, higher the frequency, lower the voltage obtained, and the opposite is also true. In the particular case of the PIII in tubes, once the plasma ignition condition is reached (stable voltage and current), it is difficult to change substantially the implantation conditions (for instance, we could not increase the voltage from 2 to 5 kV, say, or the current from 5 to 10 A, even by changing the primary current substantially).

The vacuum chamber consists of a 600 liter SS cylinder (40 cm radius by 1200 cm long), with various windows, built by the FCA company, which can be pumped down to the 10^{-6}–10^{-7} mbar pressure range by a set of mechanical, root, and diffusion pumps supplied by Edwards company. Gases are injected using a MKS flow meter (up to 20 SCCM) and glow discharge plasmas can be typically generated inside the tube by pulsing it under the presence of 2-4 $\times 10^{-2}$ mbar pressure gas, or by a more general scheme in which a DC glow discharge with hot filament addition can be ignited inside the whole vacuum chamber. In the present experiments, no DC glow or filament heating is necessary, only the H.V. pulses in the tube, but they can be used for experimental result comparisons of these different cases in the future, if necessary. Concerning

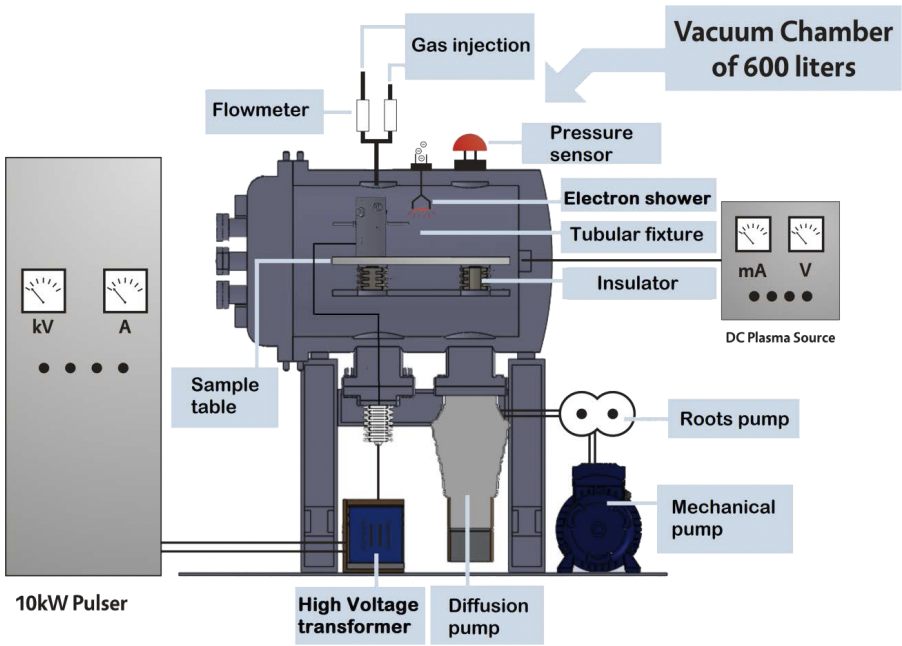


FIG. 1. Bird's eyes view of the PIII system used in the present experiment.

the pressure variations, if it is much lower than $2–4 \times 10^{-2}$ mbar, the implantation condition stability is lost (V and I waveforms are distorted which poses danger to the pulser). On the other hand, we avoided too much high pressures (e.g., over 6×10^{-2} mbar) because of the range of adequate functioning of the diffusion vacuum pumping system being used.

Surface analysis of the SS304 samples treated by nitrogen PIII inside the tube fixture was carried out by XRD to identify the new γ_N phase formed after PIII, by nanoindentation to measure the surface hardness and by GDOES (Glow Discharge Optical Emission Spectroscopy) for the obtained nitrogen implantation profiles. Raman spectroscopy (Renishaw 2000) provided D and G peaks indicative of DLC deposition on the inside walls of the fixture, represented by both Si and SS304 samples placed there. Dummy screw heads were also DLC covered, indicating successful PIII and D processing of components inside such a conductive tube. XRD was performed using a diffractometer Panalytical (X'pert Powder model) in a standard Bragg Brentano configuration with Cukα (λ = 15 406 Å) radiation, nanoindentation with a Nanoindenter XP (MTS), and GDOES with a GD profiler from Jobin Yvon-Horiba manufacturer. The micrographs were obtained by Scanning Electron Microscopy (SEM) using JEOL equipment (JSM-S310). A fast camera from Photron company, model FASTCAM, 1024PCI series, was used for the frontal and lateral imaging of the plasma produced inside the tube.

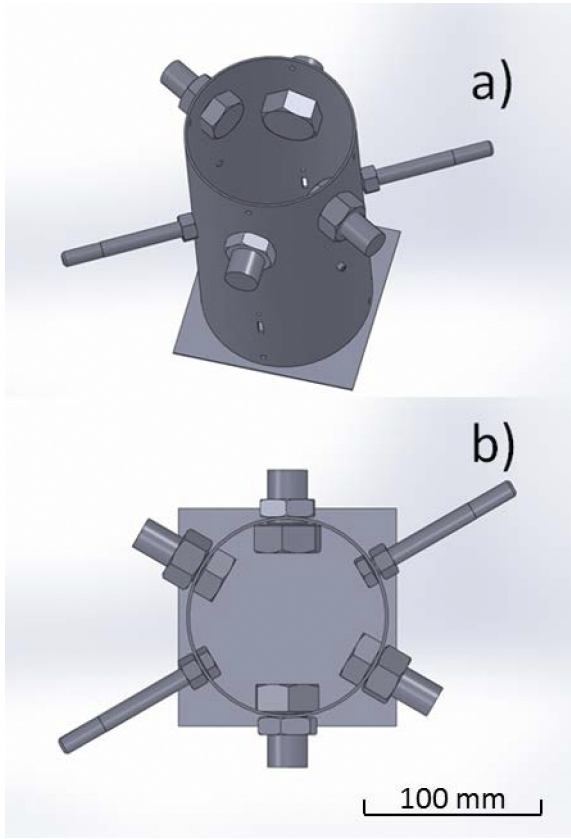


FIG. 2. Set-up of the SS304 tube fixture loaded with some of the three-dimensional components with parts to be implanted inside the tube. (a) View in angle. (b) Top view.

III. PROOF OF PRINCIPLE EXPERIMENTS AND RESULTS

The main idea of the new method of PIII and PIII and D developed by the authors is depicted in Figures 2(a) and 2(b). The hollow cylindrical fixture is made of a SS304 tube of practical diameter (10–20 cm), length (around 20 cm) and thickness (about 2 mm). Of course, other appropriate tube sizes could be used depending on the applications and pulse power capability. Low intensity magnetic field (order of 100 gauss) could also be added as in our other previous experiments but in this first attempt it was not used. If the workpieces are of simple shape, flat, not so large or too thick, they could be ordinarily assembled inside the whole fixture tube wall. If the workpieces are knives with sharp edges (to keep them sharp), it is necessary to expose only their edges to the plasma through slits in the tube, for instance. If they have more complex three dimensional shapes, like spheres, then they have to be fixed from the outside of the holes in the tube, and partially treated in several steps.

Most of the times, however, industrial parts require treatments of only a small portion of the whole body.[21] Then, it is possible to assemble them around the tube, as shown in the drawings of Figures 2(a) and 2(b), only exposing the parts of interest of the workpieces to the plasma. In the schematic drawing, we can see the branch-like feature of parts of the workpieces sticking out of the tube wall, as in small tree trunks without leaves. Since the parts unexposed to plasma staying outside the tube are of no concern, they just stay untreated (or negligibly treated) and do not take part in the PIII or PIII and D process. Contrary to the conventional form of batch processing with many metal branches holding the components,[1] the assembling of the parts to be treated becomes much simpler and in many cases, with more efficient results. Virtual leakages in the fixture are easily avoided and related vacuum problems are minor. Various tube fixtures could be connected in series for even higher outputs if higher power pulsers are used. In the present set-up, a metal plate partially covers the bottom of and is connected electrically to the tube to avoid deposition of sputtered material over the insulator surface which could lead to arcs after long treatments (as discussed later).

Additional advantages of this tube fixture method over the traditional PIII and PIII and D are the following: (a) No additional plasma source is required, other than the plasma produced by the high voltage pulser of reasonable power (>10 kW); (b) the plasma source is located inside the tube, therefore, less heating of the vacuum chamber walls occurs, as well as, less cleaning of the chamber is necessary after the treatments (especially crucial for traditional PIII and D processes which cause depositions everywhere inside the chamber which requires cleaning after each treatment); (c) secondary electrons are confined to inner side of the tube mainly, helping to increase the plasma density and implantation current, hence improving the PIII or PIII and D performance; (d) because of high plasma density, small sheath thickness is present around the exposed parts (in many cases the sheath sizes would be much smaller than the whole body sizes) of the workpieces; (e) because of the reduced dimensions of the exposed parts of workpieces, they almost become part of the tube inner

wall, hence the corresponding sheath is less prominent, reducing considerably the restrictions for the criteria of sheath overlapping in ordinary batch processing in PIII and PIII and D; (f) since a smaller area of the workpiece is treated (only the needed part), the cost and the treatment times of PIII and PIII and D processing become reduced; (g) easier assembly of parts in the tube fixture outside the chamber is possible and subsequently, the whole system to be pulsed can be positioned adequately inside the vacuum chamber; (h) smaller vacuum chambers are required for the new PIII and PIII and D batch processing systems, for the same throughput; and (i) moderate temperatures (300–400 °C) can be achieved rapidly in this configuration (if high power pulsers are used), allowing the production of thick treated layers in steel components.

There are some disadvantages of this new method however (a) not adequate for very large, very complex, or very heavy workpieces requiring their whole surface treatment, (b) it requires higher power (typically >10 kW), and output current (>20 A) pulsers, (c) since plasma production and implantation of ions are carried out with the same power supply, their independent control is not possible, sometimes lowering the implantation energy or reducing the implantation period during the pulse, and (d) the required operation pressure is reasonably high (typically $>2 \times 10^{-2}$ mbar) for maintaining the discharge on inner side of the tube, hence the plasma may become collisional which is not so desirable for ion implantation efficiency.

According to Sheridan,[22] the ion matrix overlap length is given by $D = \sqrt{-4\varepsilon_0 \emptyset_l / en_0}$, where $\emptyset_l$ is the tube potential, and n_0 the plasma density. If the radius of the bore R_b is greater than D, then, the maximum ion impact energy in the inside wall of the tube is almost the total energy applied through the pulser. In our case, we can estimate that D = 0.24 cm, while R_b = 5.5 cm, if $n_0 = 10^{11}$ cm^{-3}. Hence the condition of $R_b > D$ is obeyed easily in our case and then the largest part of the energy of the electrical pulses is applied to the ions for implantation. Such plasma densities are possible to be attained in hollow cathodes easily[23] but in our present experiment it has not being measured yet. We have not yet used the auxiliary electrode concept in this experiment either,[24] because of the favorable estimation above.

To demonstrate the viability of the idea exposed above, two specific experiments were carried out:

A-PIII with the stainless steel tube fixture with dimensions of 11 cm diameter, 20 cm length and 2 mm thickness, loaded with some industrial component dummies (various large size bolts with their heads inside the tube) (as in Figures 2(a) and 2(b)), and SS304 samples fixed in the inside walls of the tube (along its axis) using SS304 cover supports like the ones shown in Figure 3.

B-PIII with tube fixture with the same dimensions and loaded with SS304 samples only, using the scheme of Figure 3.

The photo of the fixture with dummy loads, after nitrogen plasma ion implantation, is shown in Figure 4.

In fact, for case A treatment, real industrial simulation with the fixture loaded with workpieces was tested. As the picture of Figure 5 shows, the plasma is ignited only inside the tube, with the sticking parts outside the tube not playing any function in the process. Not a single arcing occurred from

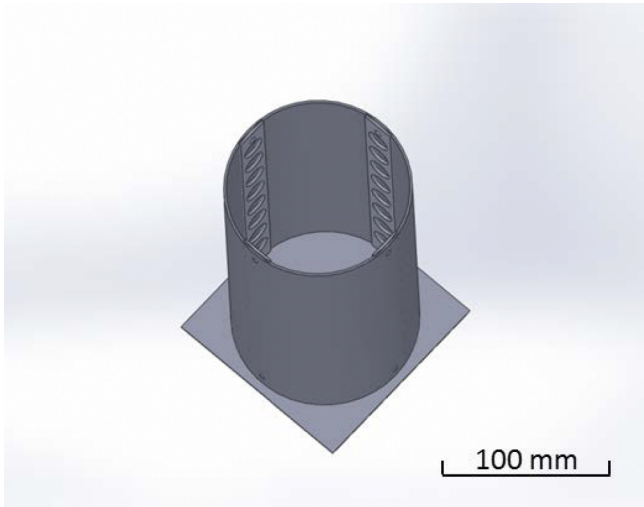


FIG. 3. Tube fixture with many samples loaded inside the tube, view in angle.

parts outside the tube despite sharp bolt screw steps. The bottom plate was crucial to run the experiments for a long time. To know how much of sputtering is occurring in this set-up is an ongoing experiment. As the picture of Fig. 5 taken by a commercial camera shows, the light emission from outside the plasma is minor, while from the inside it is very bright. The plasma shoots out in cone geometry, as seen in the picture. Indeed, recently taken fast camera images (front image of the tube) show more clearly this fact. These images are not shown here but are included in the next paper. We have not taken measurements of ion implantation outside the tube yet by, say AES or GDOES of samples there but this will be confirmed later. No arcs were seen (visually, or in the voltage x current waveforms) outside the tube despite many sharp points there. But most importantly, ion implantation inside the tube can be obtained as in normal plane supports, with similar or higher efficiencies.

Unfortunately or not, we are not being able to increase the voltage above, say, 3 kV, when running the discharge inside the tube with our present high voltage pulser. This low voltage operation limit is one of the reasons we do not get arcs. Another reason is the fact that most of the plasma occurs inside the tube while the sharp points outside are far from the ground. We have seen some small arcs at the contact points between

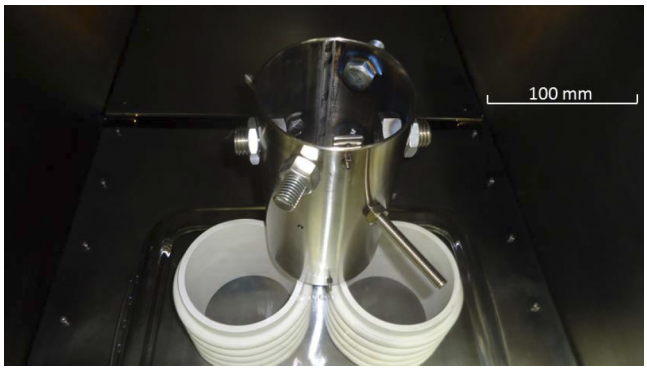


FIG. 4. Photo of the tube fixture loaded with components and samples after PIII treatments.

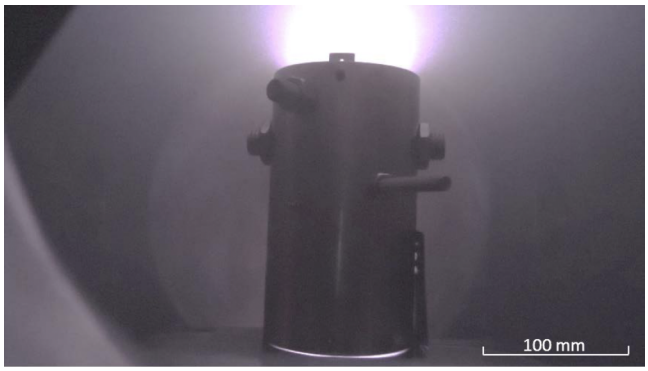


FIG. 5. Side view picture of the tube fixture loaded with industrial components during PIII treatment.

the metallic tube and the insulator (a glass structure) after some half an hour of treatment of the tube. We believe that this is caused by the deposition of the sputtered material from the tube and workpieces under treatment. This problem was avoided by placing a metallic sheet cover between the tube and the insulator which blocked the deposition.

The treatment conditions of workpieces and SS304 samples are reported in Table I. The temperature of the tube at the center height changed gradually from ambient to 340 °C at the end of the treatment. The nitrogen pressure during the PIII operation was 3×10^{-2} mbar and the total treatment time was 120 min, preceded by 10 min Argon bombardment surface cleaning.

Nitrogen was implanted under the following conditions: 2-2.8 kV, 1 kHz, 40 μs negative high voltage pulses applied to the tube, and hollow cathode like plasma produced mainly inside the tube. It is to be noted that, from the fast camera pictures, we could also see that initially the density is low, as the emission from the plasma is low. The plasma turns on with the start of each H.V. pulse and turns off after the pulse end, this cycle being repeated at the prescribed frequency of the high voltage pulser.

Furthermore, although not shown in this paper, the results of fast camera measurements showed that the plasma is on (very bright emission), mainly during the applied pulses. The plasma emits light (very faintly) at most up to 40 μs after the end of the pulse. Since it takes about 1 ms (at 1 kHz pulsing) for the next pulse to come, the effect of the plasma on the samples during the pulse off period should be negligible.

Analysis of all the samples of SS304 distributed inside the tube and placed in the axial direction indicated that we obtained: γ_N of high intensity observed by XRD; large rugosity and surface with much higher hardness. By confirming this scenario experimentally, it was possible to prove that this new method of PIII using tubular fixture and plasma generated inside the tube by high voltage pulses works quite satisfactorily in the batch mode. And these favorable results were attained in spite of the presence of reasonably large elements sticking inside and outside the tube.

For case B treatment, since there are no parts sticking out the tube but only flat supports with samples inside it, less problems with arcing were expected, based on our previous results.[20] In fact, the experiment progressed smoothly and the samples were treated for 2 h after a surface cleaning with argon bombardment (10 min cleaning). The surfaces of the samples exposed to nitrogen bombardment were analyzed with different techniques as discussed above. The results of ion implantation obtained in these two experiments are discussed in detail, in Sec. IV.

IV. DISCUSSION

Since it is very difficult to carry out analysis of the surface of real industrial workpieces, most of the time, the fixture was loaded with SS304 samples together with the workpieces, treating them under the same PIII condition. Next, the results obtained for the treatment of case A are shown, first.

From the results of XRD measurements (Figure 6), it is clear that, in addition to the (111) and (222) initial bulk FCC γ phase, peaks of the well-known nitride expanded γ_N phase are present at any position of the samples which were placed about 4 cm from each other, in the tube axial direction. The γ_N peak positions and intensities indicate that significant nitrogen incorporation was attained. Previous experiments have shown that prominent γ_N indicated high percentage of nitrogen incorporation and diffusion into the material.[25] This was confirmed by the elemental-profile obtained by GDOES measurements, as shown later. The intensities of the γ_N peaks are reasonably similar in shape and position but a little bit different in amplitude. This is probably due to the different temperatures along the axis that were observed during the treatment (measured with an optical pyrometer), leading to slight modifications of nitrogen concentrations and diffusion depths. The positioning of the dummy components (nuts and bolts) in the fixture influences the obtained temperature and its distribution due to their mass as well as surface and volume. Therefore, a much uniform treatment is expected for better distribution load of the components (under study).

Nanoindentation performed in sample CE58 (one of the samples with XRD shown in Figure 6) resulted in the hardness profile of Figure 7. It clearly shows again the good implantation obtained in case A experiment which resulted in

TABLE I. PIII treatment conditions and temperatures achieved in the tube, for case A.

Peak Voltage (kV)	Pulse current (A)	Pulse length (μs)	Frequency (kHz)	Temperature at the center height of the fixture (°C)	Time (min)
2	5.5	40	1	275	30
2.5	5.5	40	1	315	60
2.8	5.5	40	1	335	90
2.8	5.5	40	1	340	120

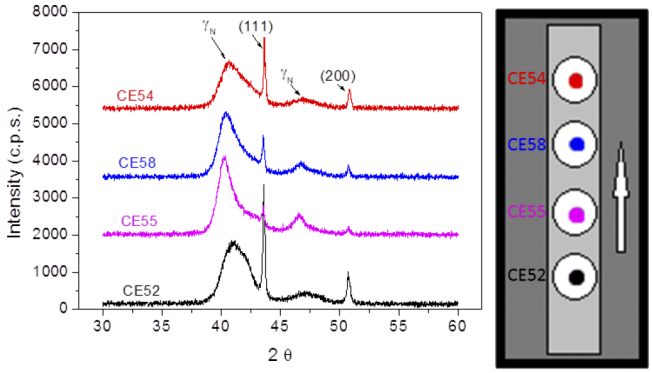


FIG. 6. XRD patterns of SS304 samples placed at different axial positions inside the tube, for case A.

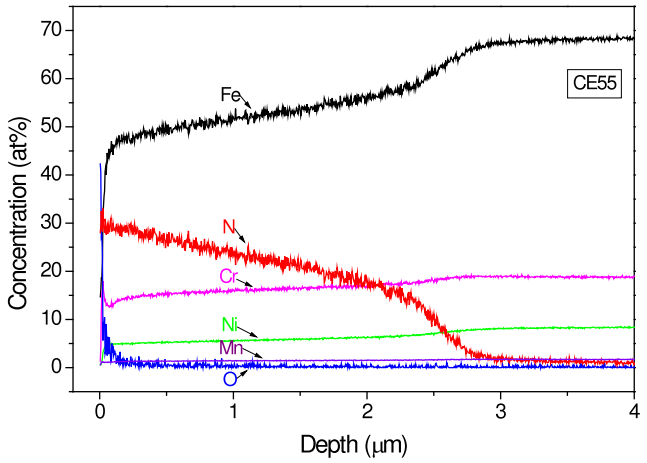


FIG. 8. Profiles of implanted nitrogen and other elements in the SS304 sample (CE-55) placed inside the tube fixture.

2.4 times larger hardness around 200 nm depth as compared to the reference sample. The hardness for the treated one was larger than that for the reference one for up to 1000 nm, which allows us to infer that diffusion of nitrogen reached about 3–5 μm, which was confirmed by GDOES measurements. The graph of the elemental profiles of Figure 8 shows that nitrogen has diffused-up to 3–4 μm, in the sample CE55, near CE58. Nitrogen atomic concentration obtained at the surface was near 30 at. %, it then slightly decreases down to 20 at. % over 2.2 μm before reaching the zero level, smoothly, for larger depths.

XRD patterns of SS304 samples placed at different axial positions inside the tube, for case B, are shown in Figure 9. The PIII treatment conditions were similar to those shown in Table I. It can be seen that the γ_N peaks are also reasonably similar to each other (as in case A) for samples placed in different axial positions inside the tube. They were located at 3.5 cm from the top, then 3.5 to the next, and so on. They indicate that good nitrogen incorporation was obtained along the tube despite not so high temperatures observed at the end of this experiment (320 °C).

There is in fact a great necessity for a detailed investigation of the sheath behavior inside the tube which will be conducted in the future. Concerning the non-uniformity of ion implantation in the axial direction, we can see the XRD signals in Figs. 6 and 9 for comparison. They differ significantly (but not massively) in both cases, with and without workpieces. We only presented the GDOES result for a single sample placed inside the tube which is shown in Figure 8 because it is very difficult to do GDOES in all the treated samples (this is performed abroad). We have done EDX (Electron Dispersive X-Ray) instead, in various samples along the axis in another treatment inside the tube and found that the relative retained dose difference measured is within 30%. Further measurements with GDOES are underway and will be reported in the next paper.

PIII and D processing was also tested in this cylindrical fixture/hollow cathode configuration. DLC was deposited on the SS304 screw heads of large to moderate sizes placed inside the tube. Firstly, a surface cleaning was performed with argon sputtering, then nitrogen was implanted in sequence for the buffer layer, and finally, acetylene was used for the DLC deposition phase. The PIII and D processing was carried out with gas pressures in the 3-5 $\times 10^{-2}$ mbar range, using 2-3 kV pulses, at 1 kHz frequency, and 30 μs duration. Total currents of 2–4 A were drawn in this setup. The plasmas of argon, nitrogen and acetylene were produced easily, and seen flowing out in a jet-like shape, only near the top end of the tube (as in Figure 5). Consequently, only the places inside the chamber (top side) facing the fixture showed some deposition outside

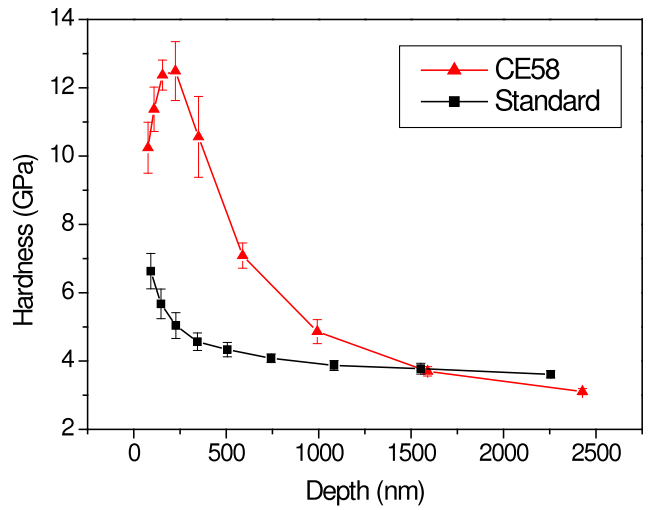


FIG. 7. Hardness of the SS304 sample treated by nitrogen PIII (CE58), in case A, and the reference sample.

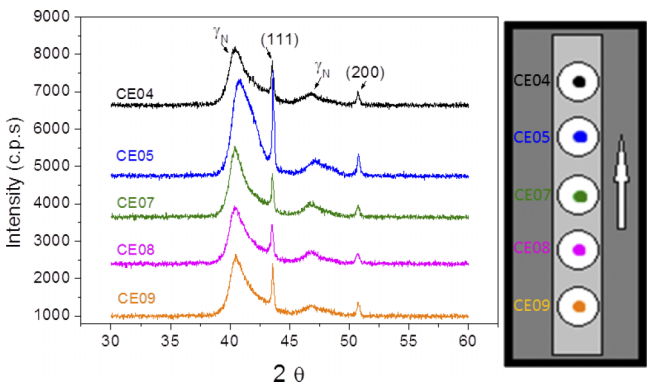


FIG. 9. XRD patterns of SS304 samples placed at different axial positions inside the tube, for case B.

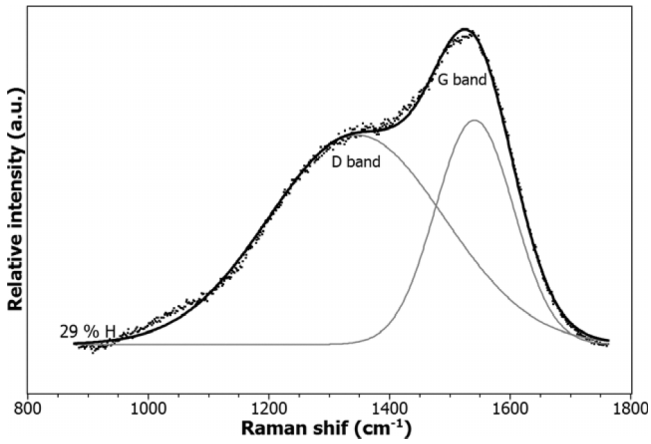


FIG. 10. Raman spectra of DLC deposited on the Si sample placed inside the tube fixture.

the tube, while the rest of them (the whole inner chamber walls) were slightly affected. This is in contrast to the cases in which we perform DLC depositions by the PIII and D method, in a small chamber, with samples exposed to plasmas filling the whole vessel. In these cases, the entire chamber needs to be cleaned each time after the experiment.

The chemical structure of the obtained DLC coatings was identified by Raman scattering spectroscopy (Renishaw 2000 system), the result of which is shown in Figure 10. The measurements were made in air at room temperature, with Ar+ laser (λ = 514.5 nm). The laser power on the sample was about 0.6 mW. The Raman system was calibrated with respect to the diamond peak in 1332 cm^{-1}. Clear D and G peaks can be seen here, and from the analysis based on the method of Casiraghi *et al.*[26] 29% of hydrogenation of the obtained DLC can be inferred in this case. Furthermore, the obtained thickness of DLC, inside the tube or Si sample surface, can be estimated from SEM cross-section images of clivaged DLC deposited Si, in Figure 11, which showed near 2 μm deposition, after 20 min of acetylene PIII and D treatment. The uniformity of the DLC deposition was of the order of 20%, within 10 cm, inside the tube. The deposited layer was thinner near the end of the tube (among 3 Si samples placed along the axis), compared to the ones at the tube center. DLC deposited on the screw heads were also analyzed by Raman spectroscopy and showed equivalent D and G peaks.

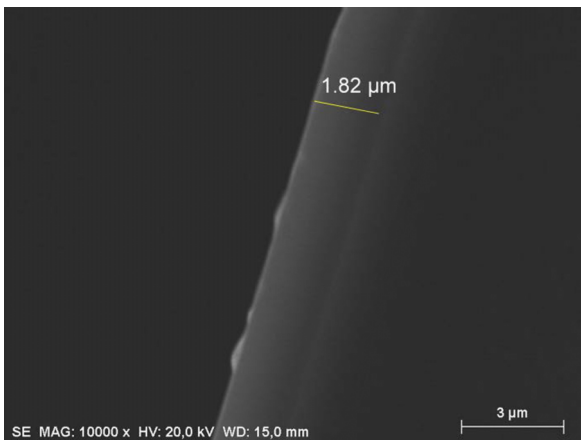


FIG. 11. SEM cross-section image of the DLC deposited on the Si wafer sample after clivage.

As a final comment, it should be added that GDOES measurements for each sample placed in different axial positions, for case A and B experiments, are underway, to solve the question of uniformity of this PIII Me-tube fixture method. Furthermore, it is necessary to say that for each material or component, an optimization of the pulse parameters will be needed, when using this method, as is the case for other batch processing methods.

V. CONCLUSIONS

In conclusion, a new method of PIII and PIII and D useful for treating industrial components in the batch mode has been devised. It consists of using a metallic tube fixture for holding the components, exposing only the parts to be treated to the hollow cathode-like plasma produced inside the tube by the negative high voltage pulses applied to the fixture, after the required gas injection. This allows the ion implantation of desired parts of the components in a much more effective way than the traditionally used method in which each component is exposed to the plasma in an individual manner and spread all over the chamber (without sheath overlapping). The analysis of the surface of the SS304 samples placed together with the dummy components showed that a significant incorporation of nitrogen (up to 3 μm depth and peak concentration of 30 at. %) was obtained which caused an increase of up to 2.4 times in their hardness. This new method can be used for PIII and D treatments also, which was confirmed for DLC depositions inside the tube as well as in dummy loads of SS304 screw heads placed there. Furthermore, it was shown that less cleaning inside the chamber after the DLC depositions was necessary, and the PIII and D treatment was quick and highly efficient. Finally, we expect that our method (tubular fixture/hollow cathode) can also be extended to other more traditionally used batch processing methods in CVD plasmas or plasma nitriding at low pressures.

ACKNOWLEDGMENTS

We thank the efforts of Ms. C. Sara Blunk from UFPR, Brazil for the nanoindentation results, the drawings of the PIII device and fixtures with samples and components by Mayse Maciel dos Santos from INPE, Brazil, the help from Dr. M. M. Silva from ITA, Brazil for GDOES measurements, assembling and operation of the PIII device by Matheus M. N. F. Silva from INPE, Brazil, and the funding from Brazilian agencies of CNPq and MCTI.

[1]A. Anders, *Handbook of Plasma Immersion Ion Implantation and Deposition* (John Willey&Sons, New York, 2000).
[2]M. Ueda, L. A. Berni, R. M. Castro, A. F. Beloto, E. Abramof, J. O. Rossi, J. J. Barroso, and C. M. Lepienski, Surf. Coat. Technol. **156**, 71 (2002).
[3]R. M. Oliveira, J. A. N. Gonçalves, M. Ueda, G. Silva, and K. Baba, *Proceedings of the 9th International Conference on Protection of Materials and Structures from Space Environment* (American Institute of Physics, 2009), pp. 357–367.
[4]P. K. Chu, J. Y. Chen, L. P. Wang, and N. Huang, Mater. Sci. Eng., R **36**, 143 (2002).

[5]A. M. Staines and T. Bell, Thin Solid Films **86**, 201 (1981).
[6]T. Ohana, T. Nakamura, M. Suzuki, A. Tanaka, and Y. Koga, Diamond Relat. Mater. **13**, 1500 (2004).
[7]B. Terreault, Surf. Coat. Technol. **156**, 13 (2002).
[8]R. Wei, Surf. Coat. Technol. **204**, 2869 (2010).
[9]X. Zeng, B. Tang, and P. K. Chu, Appl. Phys. Lett. **69**, 3815 (1996).
[10]K. Baba and R. Hatada, Surf. Coat. Technol. **741**, 158-159 (2002).
[11]M. Ueda, L. A. Berni, G. F. Gomes, A. F. Beloto, E. Abramof, and H. Reuther, J. Appl. Phys. **86**, 4821 (1999).
[12]G. A. Collins, R. Hutchings, K. T. Short, and J. Tendys, Surf. Coat. Technol. **212**, 103-104 (1998).
[13]N. Sakudo, D. Mizutani, Y. Ohmura, H. Endo, R. Yoneda, N. Ikenaga, and H. Takikawa, Nucl. Instrum. Methods Phys. Res., Sect. B **206**, 687 (2003).
[14]I. G. Brown, Rev. Sci. Instrum. **65**, 3061 (1994).
[15]M. Ueda, M. M. Silva, C. M. Lepienski, P. C. Soares, J. A. N. Gonçalves, and H. Reuther, Surf. Coat. Technol. **201**, 4953 (2007).
[16]V. Fouquet, L. Pichon, A. Straboni, and M. Drouet, Surf. Coat. Technol. **186**, 34 (2004).
[17]R. M. Oliveira, J. A. N. Gonçalves, M. Ueda, J. O. Rossi, and P. N. Rizzo, Surf. Coat. Technol. **204**, 3009 (2010).
[18]E. J. D. M. Pillaca, M. Ueda, K. G. Kostov, and H. Reuther, Appl. Surf. Sci. **258**, 9564 (2012).
[19]S. F. M. Mariano, E. J. D. M. Pillaca, M. Ueda, and R. M. Oliveira, Surf. Coat. Technol. **256**, 47 (2014).
[20]E. J. D. M. Pillaca, M. Ueda, S. F. M. Mariano, and R. M. Oliveira, Surf. Coat. Technol. **249**, 104 (2014).
[21]M. Ueda, L. A. Berni, and R. M. Castro, Surf. Coat. Technol. **200**, 517 (2005).
[22]T. E. Sheridan, J. Appl. Phys. **74**, 4903 (1993).
[23]D. M. Goebel, K. K. Jameson, R. M. Watkins, I. Katz, and I. G. Mikellides, J. Appl. Phys. **98**, 113302 (2005).
[24]P. Wang, X. Tian, C. Gong, S. Yang, and P. K. Chu, IEEE Trans. Plasma Sci. **39**, 3120 (2011).
[25]M. Ueda, G. F. Gomes, E. Abramof, and H. Reuther, Surf. Coat. Technol. **186**, 291 (2004).
[26]C. Casiraghi, A. C. Ferrari, and J. Robertson, Phys. Rev. B **72**, 085401 (2005).