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Experiments on plasma immersion ion implantation inside conducting tubes embedded in an external magnetic field

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ABSTRACT

Tubes of stainless steel (SS) embedded in external magnetic field were used to study the effects of plasma immersion ion implantation (PIII) as a function of their diameter. The study was complemented with and without a grounded auxiliary electrode (AE) placed at the axis of the tube. During the discharge tests in tubes of larger diameter (D = 11 cm), with and without AE, nitrogen gas breakdown was established inside the tube at pressures near 2.0×10^{-2} mbar. Under the same operation conditions, stable plasmas with similar PIII current densities were obtained for both arrangements. Reducing the diameter of the tube (D = 1.5 cm) turned the plasma unstable and made it inappropriate for ion implantation. This situation was solved by supplying gas at higher pressure or using higher magnetic field, without the presence of an AE. Under these conditions, nitrogen PIII treatments of these small diameter tubes were performed but gave not the best implantation results yet. Our results have also shown higher ion implantation current density (16 mA/cm^2) in tube of intermediate diameter (D = 4 cm) using AE, compared to largest diameter tube used. In this case, a thick nitrogen layer of about 9 μm was obtained in the SS sample placed inside the tube. As a consequence of this, its structural and mechanical properties were enhanced. These results are attributed to the thermal diffusion promoted by ions hitting the inner wall in a large number due to the presence of the AE and the magnetic field.

1. Introduction

Treatments inside metallic tubes are being widely studied nowadays due to its broad utility and practical importance for fluid transports, in general. Actually, several methods of surface treatment are being used to enhance the resistance against corrosion and wear in tubes. Among the several techniques used for this goal, treatment based on plasma such as plasma immersion ion implantation stands out.

Plasma immersion ion implantation (PIII) is a well-established method, used mainly for the three-dimensional surface modification of materials [1–3]. However, in the treatments of workpieces for industrial applications with concave geometry, such as piston rings, tubes, pipes, etc., poor implantation has been obtained so far [4]. It was pointed out in the literature that a lower ion energy than expected occurs during ion implantation. Sheridan has attributed this behavior to the decrease of the applied electric potential which is related with the important scale length called the ion-matrix overlap, $d = \sqrt{-4\left(\epsilon_0 \phi / e n_0\right)}$ and the bore radius, R [5,6]. It has also been shown that by inserting a grounded conductive auxiliary electrode (AE) along the axis, the average ion impact energy can be recovered [7]. However, this is not heartening when AE is tried inside tubes with small R due to problems of electric insulation. Consequently, generation of plasma inside tubes with short diameters is difficult to take place and new methods as electron cyclotron resonance (ECR) microwave discharge were proposed [8].

Another important aspect studied in tubes was the dependence between the tube diameter (D) and its length (L), on plasma density [9]. The studies demonstrated that plasmas with critical densities occur at $L \gg D$. In the same sense, investigations about dose implanted inside tube were related to aspect ratio D/L. Numerical investigation revealed that ions coming from outside tube contribute to the implantation [10,11]. In this study, it was shown that ions pass through the middle of the tube and arrive at the end of it when short length, $L \sim D$, is used. That behavior does not occur if tubes have long enough length, $L \gg D$. Therefore, effects of the

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ions implanted nearby the end of the tube promote a non-uniform dose along the inside of the tube. This situation is critical, thus additional setup were proposed to improve it [8,9,12]. By use of a grounded cylindrical grid electrode inside tube, reasonably uniform dose was obtained [9]; however, its use is limited to short diameter. This restriction is surpassed by the combined application of ECR and magnetic field [8,12]. In this method, the plasma is made to move along the axis direction during treatment to obtain a uniform dose; however a complicated system and intense magnetic field are required. Knowledge of these issues is of great importance to try achieving implantation with great uniformity but it still remains a challenge to date.

In particular, the use of a simpler external magnetic field can be an option in order to overcome part of these limitations. Recently, application of magnetic bottle configuration in PIII in materials proved to be more suitable for the improvements of the surface properties in relation to the conventional PIII [13–15]. In this process, a system of crossed $E \times B$ fields is produced around the target by application of transverse magnetic and electric fields during the PIII. The use of this configuration allows obtaining high plasma density due to intense background gas ionization by the trapped electrons [16]. Thus, a high ion flux hitting the target is obtained making it possible to rise the temperature on it. As a consequence, the mechanism of thermal diffusion is set-up, allowing thick nitrogen layer, at a relatively short treatment time compared to other conventional methods used for the same goal. In fact, this advantage is now being used for the formation of DLC film [17] and for the treatments inside conducting tubes [18]. Taking advantage of these recently obtained improvements, in this work, PIII process using $E \times B$ fields was tested in tubes of Stainless Steel with different diameters.

2. Experimental details

The experimental arrangement of PIII with tubes embedded in external magnetic field is shown in Fig. 1. The experiment was carried out in a cylindrical vacuum vessel with 38-cm length and 26-cm diameter. For generation of the axial magnetic field, four magnetic coils were mounted on the outer side of the PIII cylindrical chamber. The coils were wound to form a magnetic bottle type configuration, that is to say, a region with one magnetic field minimum in the center of the chamber and maximums near the coils. The point of minimum field was chosen to coincide with the place where the tubes were positioned.

Three tubes made of stainless steel (SS) of 15 cm-length and diameters of 11 cm (larger), 4 cm (medium) and 1.5 cm (smaller) were prepared for the experiments, including the possibility of positioning an AE of 0.4 cm-diameter inside. The tubes were connected electrically to the high voltage feed through (see Fig. 1) whereas the AE was grounded.

To monitor the effects of ion implantation on the inner wall of the tube, Silicon and SS samples were prepared. SS304 samples were chosen due to its similar composition of the tubes whereas Silicon samples with (1 0 0) orientation were used for comparison purpose with SS samples. SS disks with 0.3-cm thickness and diameters of 1.0 cm and 1.5 cm were sand papered using silicon carbide paper in a series of 350, 500 and 1200 grit and subsequently a 0.5 μm alumina in liquid solution was used for final polishing. We used 0.5 mm thick and 1.5 cm × 1.5 cm pieces of commercial Si wafer which was subsequently chemically cleaned. Afterwards, SS and Si samples were cleaned in ultrasound with acetone and deionized water before treatment. After this, seven SS and Si samples were mounted on Sample Holder (SH) of 15-cm length and then placed on the tube inner wall for the tubes with medium and large diameter. For the tube with smaller diameter,

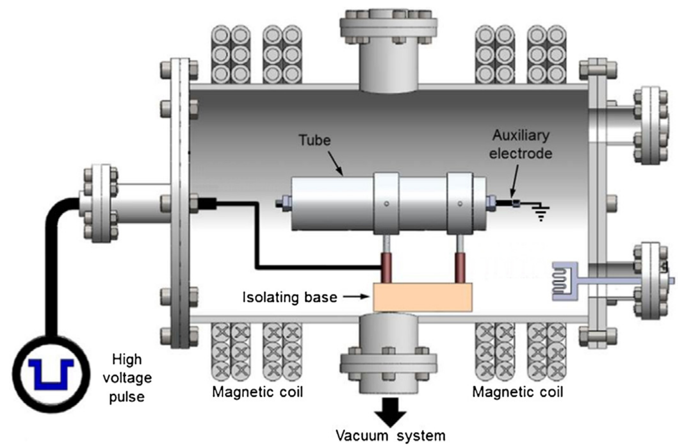

Fig. 1. Schematic diagram of the PIII experimental setup.

additional arrangements were mounted outside it to place the SH. The base pressure set by mechanical and diffusion pumping was about 4.0×10^{-5} mbar, while nitrogen working pressure of $2–4 \times 10^{-2}$ mbar was used throughout the treatment. Negative voltage pulses of 6 kV amplitude, 20 μs duration and 500 Hz frequency were applied at the tube for ion implantation. The total current on the tube was measured with a Rogowsky coil. Depending on the diameter of the tube, the magnetic field was set between 45 G and 90 G. Finally, the PIII treatments were performed for 60 min.

Experiments in smaller tube using AE had caused some difficulties (instability of the plasma turn on) during the test of electrical discharge. Due to this, results for $D = 1.5$ cm with AE are not exhibited in this work.

Treated and untreated SS samples were analyzed using different characterization techniques. These were performed in samples placed in the middle of the inner surface of the tube. Nitrogen concentration profiles versus depth were measured according to thickness. For thicker layers: Glow Discharge Optical Emission Spectroscopy (GDOES) was performed using a Jobin–Yvon–Horiba GD-Profiler at a sputtering rate of 0.07 μm s^{-1}. For thinner layer: high resolution Auger Emission Spectroscopy (AES) was performed using an equipment from FISONS Instruments Surface Science, model MICROLAB 310-F, at a sputtering rate of 0.3 nm s^{-1}. The structural changes in the surface layer were investigated by X-ray diffraction (XRD) in a Bragg–Brentano geometry with *CuKα* radiation. The surface hardness of the samples was obtained using a Nanoindenter XP (MTS Instruments). An infrared thermometer Micron model M90 with range between 250 °C and 2000 °C was used to monitoring the temperature on the tube, during PIII. The characteristic voltage and current wave-forms were recorded using a digital oscilloscope Tektronix model TDS360 for further analysis.

3. Results and discussions

Prior to ion implantation inside the tubes of large, medium and small diameters, some aspects related to the breakdown and maintenance of the discharge for PIII embedded in magnetic field were analyzed, for cases with and without AE.

The first test was conducted in tube of $D = 11$ cm without AE. Here, the voltage and the magnetic field were kept at 6 kV and $B = 45$ G, respectively, to find the gas breakdown point by gradually increasing the gas pressure from 8×10^{-3} mbar to 6×10^{-2} mbar. For $p = 8 \times 10^{-3}$ mbar, formation of the plasma occurred outside the tube, preferentially. This effect can be explained by the efficient ionization of the residual gas promoted by the special distribution of the $E \times B$ fields surrounding the tube [16,19]. By increasing the gas pressure to up to near 10^{-2} mbar, an unstable plasma was obtained