Deposition of materials using a plasma focus of tens of joules

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Abstract. Physical properties of transient plasmas, energetic ions and electrons, as produced in plasma focus (PF) discharges are substantially different than the conventional plasma devices used for plasma nanofabrication. In particular, PF discharges provide new and unique opportunities in processing and synthesis of new materials. Since PF discharges have very short duration and produce plasmas of high ion density, the anode is exposed to a high energy density causing its pulverization and generating a vapour of material that allows a fast deposit. In this paper a table top plasma focus of tens of joules, PF-50J, was used to produce material deposition. First deposits obtained from detached anode material (steel) or a metallic insert (titanium) from the plasma ejected after the pinch in the axial direction are presented.

1. Introduction

In the last decade, there is evidence of the increasing interest in the study of small and compact plasma focus (PF) devices [1] and their various applications [2]. Specially they have attracted great interest due to the possible applications in different technological fields where you can take advantage of the fact that these devices are not only a source of high density and temperature plasmas, but also a rich source of high-energy ions usable for modification of surface properties of thin films deposition, doping of semiconductors and production/coating of nanocomposites [3-15].

The material deposition through a pulsed plasma device, such as a PF, has some special features in comparison with other methods which makes them very appropriate for the generation and treatment of technological materials. These special features include high deposition rate; an energetic deposition process; the ability to operate at high frequency; and the low operating costs. Nevertheless, these methods still require further studies to improve the quality of the resulting surfaces [7].

The dynamic of a PF allows the formation of a column of plasma of high temperature and high density at the end of the of radial collapse phase. This plasma column is then disintegrated due to plasma instabilities, generating a plasma burst of high ion density and beams of relativistic energy ions and electrons that are accelerated in the direction of the axis of the plasma column in both directions. Then, this plasma burst and energy charged particle beams, are responsible for both a possible ablation of the anode and its subsequent material deposition on a substrate, and a possible direct chemical deposition on a substrate placed at some height on the same axis.

The present study focuses on the use of the PF-50J [17, 18] device for material deposition, as well as the study of the first deposits which can be obtained from material removed from a steel hollow anode or from a titanium insert, through the plasma ejected in the axial direction. Deposits at different distances measured from the tip of the anode were obtained and characterized. Morphological and
Elemental characterization is performed by means of Scanning Electron Microscopy (SEM) with Energy-dispersive X-ray Spectroscopy (EDX), and the structural characterization through X-ray Diffraction (XRD).

2. Experimental setup and diagnostics

The experiments presented here were performed in a low-energy plasma focus designed and built in our group. This device operates at energy levels of tens of Joules (32-72J of energy stored in the capacitor bank), 160nF, 38nH, 20-30kV, maximum current of 40-60kA reached in 150ns [18].

The main vacuum chamber of the PF-50J was fitted with a sample holder and a shutter, both externally manipulated, to control the position (height from the anode, “d”) of the sample and the pulses of deposition respectively (See Figure 1). Discharges were conducted at a pressure of 6 mbar of hydrogen gas and with a charging voltage of 28 kV. The PF-50J was operated with hollow steel anodes of different depth and inner diameter. The discharges for depositions were made at a variable distance between the anode and substrate and accumulating 100 continuous discharges in each case.

![Figure 1: Schematic diagram of the improved PF-50J showing the moment of the pinch.](image)

As standard in-situ electrical diagnostics during plasma pulses (see Figure 2), the voltage $V(t)$ was measured with a fast resistive divider, and the current derivative $dl(t)/dt$ with a calibrated Rogowski coil. A photomultiplier was implemented to detect x-rays emitted from the pinch compression, and monocrystalline silicon wafers were placed within the chamber, as substrates to deposit the generated material.
3. First results and discussion

3.1. Deposition with a steel hollow anode

Four silicon substrates were exposed to plasmas generated using a steel hollow anode. The deposits are shown in Figure 3 and their experimental conditions are detailed in Table 1.

![Figure 3: Images of the deposited samples. Dimensions: (1) 12.8x12.3; (2) 12.9x14.7; (3) 9.3x6.3; (4) 6.6x6.6 mm.](image)

Table 1: Experimental differences of samples deposited with hollow anode.

| Nº | Sample height (mm) | Anode inner diameter (mm) | Anode depth (mm) |
|----|--------------------|---------------------------|------------------|
| 1  | 16                 | 5.2                       | 10.9             |
| 2  | 21                 | 5.2                       | 10.9             |
| 3  | 14                 | 4.6                       | 18.7             |
| 4  | 14                 | 5.2                       | 10.9             |

Observing the foregoing images some differences in color and amount of deposited material can be clearly seen. Samples (1) and (2) for example, are those with less material: their appearance is rather amorphous, seems smooth and the colors that stand out of the deposit range from light brown to some blue with touches of green. While samples (3) and (4) clearly have a larger amount of material on the substrate, their appearance is more roughened and a dark metallic color is present, whose edges exhibit
similar colors to those of samples (1) and (2). With these observations is possible to determine an increase in the obtained amount of material when the substrate height is decreased, as well as larger increase with the decrease in the anode inner diameter.

Surface morphology of the deposited material with different anode geometry was imaged with a TESCAN Vega 3 LMU Scanning electron microscopy. The morphological features of the samples are shown in Figure 4. The images from sample (3) and (4) present some cracks, revealing that the samples placed closer to the anode also receive a larger proportion of the plasma shock attack, as shown in previous articles [19, 20].

Figure 4: SEM images of the center of the deposited samples from a hollow anode PF.

EDS was used to investigate the elements that are present in the deposited material. The spectra obtained for all the samples are similar in nature presenting only elements that correspond to the steel of the anode. The observation confirms the hypothesis of ablation of the anode and deposition on the substrate surface. The spectra obtained from the samples reveal that between 6% and 14% of material (in standardized atomic concentration) corresponds approximately to the elements of steel (~ 70% Fe, 20% Cr and 10% Ni) and its concentration decreases near the edges of the deposition.

Structural characterization of the deposited material with different anode geometry was made by a SIEMENS D5000 X-ray Diffractometer. The patterns obtained exhibit the diffraction peaks related to
different compounds from Fe-Cr-Ni-Si which not only confirm the EDS result about the ablation of the anode, but also the ablation of the Si wafer surface by energetic ions and their re-solidification on the substrate surface, as presented in previous work [21].

3.2. Deposition with a titanium insert

By implementing a hollow anode (inner diameter of 5.2 mm and 10.9 mm depth with a solid insert of titanium (Ti) of about 5 mm diameter) three other deposits were made. See images in Figure 5 and experimental differences in Table 2.

![Figure 5: Images of deposited samples. Dimensions: (3) 13.3x8.1; (4) 11.3x8.6; (5) 6.7x8.3 mm.](image)

| Nº of sample | Sample height (mm) |
|--------------|-------------------|
| 3            | 12                |
| 4            | 17                |
| 5            | 14                |

The above images show clear differences of the deposit obtained compared with the samples in Figure 3. The deposit presents a bright metallic silvered color with a rough appearance in the center and a smoother appearance around the edges, without the brown and blue colors seen in the previous case (just hollow anode). It seems that those colors are possibly due to the anode material of thinner layers (stainless steel). The silvered color can be distinctively associated with the titanium insert since for the samples with the expected steel deposition, the metallic appearance is darker than in the samples with the expected titanium deposition.

The morphological features of the samples imaged by SEM are shown in Figure 6. The images from sample (3) y (5) present some cracks, reproducing the same effect as in the above samples (Figure 4): closer to the anode the samples receive a good proportion of the plasma shock attack, independently of the material that is deposited or if there is an insert on the anode. Also on the images of samples (3) and (5) the melting of surface material due to the plasma attack can be distinguished.
The spectra obtained with EDS for all the samples are similar presenting only elements that correspond to titanium from the insert and a bit of the steel from the anode. This observation confirms the hypothesis of ablation of the anode and deposition on the substrate surface as in the previous case. The spectra obtained for the samples reveal (Figure 6): (3) The center of the sample contains around 7% of material that correspond to Ti and 18% of Ti and 5% of elements from steel (Fe & Cr) around the edges; (4) Near the center of the sample it contains around 15% of material that correspond to Ti and around the edges there is 28% of Ti and 5% of elements from steel (Fe & Cr); (5) The center of the sample contains around 12% of material that correspond to Ti and around the edges contains 34% of Ti and 3% of elements from steel (Fe & Cr). Combining these data it can be determined that the deposition of the anode edges (in this case steel) is much less than the one that comes from the center (Ti insert). In addition, considering that the discussed melting of the surface material due to the attack promotes a smoother surface allowing more penetration of response in the EDS spectra and thus more silicon partial percentage, we can conclude that higher relative percentage of titanium is deposited when the sample is placed closer to the anode. The latter could be explained after observing how the titanium does not seem to have a great expansion as we move the sample away from the anode. In the case of steel it is clearly spreading which means that the material comes to the sample with less energy.

Figure 6: SEM images of the center of the deposited samples from a hollow anode PF with Ti insert.
than the titanium. Considering that the ejected plasma and particles are mainly in the axial direction, if we place a sample near the anode, the trajectory of the material is shorter which means that it has less probability of interaction with the gas until deposition and can go directly to the silicon wafer. If the sample is placed far from the anode, the material collected could be less because it has the possibility to expand radially.

The XRD patterns obtained for these samples exhibit diffraction peaks mainly related to Ti (not sample (3)) or different Ti-Si (for example TiSi$_2$ or Ti$_5$Si$_3$), which again confirms the ablation of the Si wafer surface by energetic ions and its re-solidification on the substrate surface generating an interlayer and even presenting a possible limit in which the deposition of pure Ti over the interlayer starts.

4. Conclusions

We demonstrate that thin films of Ti, different Ti-Si composites (for example TiSi$_2$ or Ti$_5$Si$_3$) or compounds from Fe-Cr-Ni-Si can be deposited using a table top plasma focus device of only tens of joules. From our knowledge, it is the first time that this kind of plasma focus device, with low operating costs and the ability to operate at high frequency, has been used for thin film deposition. Nevertheless, this method still require further studies to improve the quality of the resulting surfaces.

It was observed an increase in the deposited amount of material when the height between anode and sample is decreased, as well as an increase in the deposited amount when a smaller inner diameter of the hollow anode was used. Furthermore, the samples placed closer to the anode receive a larger amount of plasma shock attack, presenting some cracks or even melting of the surface material independently if they were deposited from a hollow anode or from an insert. The ablation of the anode and its deposition on the substrate was confirmed. Also at the time of the deposition there is an ablation of the Si wafer surface by energetic ions that permits its re-solidification on the substrate surface and can form compounds generating an interlayer. However, it was observed that the deposition of the anode edges (steel) is much less and comes to the sample with less energy than the one that comes from the center (Ti insert) implying that the material coming from edges of the anode is removed by a different mechanism than the material of the center.

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