

ENHANCED IMPLANTATION AND DEPOSITION OF METAL IONS BY IMMERSION IN SYNCHRONOUS MODULATED RF – DRIVEN PLASMA

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Abstract. An improved ion source based on synchronous enhancement of RF-driven plasma by superimposed high voltage pulses is tested for metal ion implantation on non-metallic surfaces. The results were compared to metal ion implantation by immersion in classical RF plasma. It was demonstrated that using the improved ion source, the metal layer is more compact and less contaminated and a larger amount of implanted ions can be found in the non-metallic substrate.

Key words: Modulated RF plasma, ion implantation and deposition, XPS surface analysis.

1. INTRODUCTION

Plasma immersion ion implantation is a well-developed technique for introducing ions into a material specimen aiming to enhance the surface properties of advanced materials. This method of implantation is widely used for improving mechanical properties (hardness, adhesion, wear, friction, fatigue, etc.) of various kind of materials like polymers [1, 2] or dielectrics. The method can be also used to improve chemical properties, optical properties [3], electronic properties [4] and biocompatibility properties (applicable to human prostheses). Therefore, a rising interest to optimise this technique is observed and new experimental configurations have been developed [5, 6].

As the ion dose implanted, the main characteristic of the ion implantation process, increases with background plasma density [7], raising the plasma density while keeping the pressure as low as possible is desirable.

On the other hand, specimens of large surface area demand an enormous amount of ion current from the plasma during application of the negative bias. As in most cases the rate and mechanism of plasma production is independent of the bias conditions of the specimen, there can be a drop in the plasma density during the application of the bias for large areas of the specimen. S. Mukherjee [8]

analytically investigates the consequences of this drop in density on sheath expansion and ion flux using quasi-static expansion of Child's law. The results indicate a drastic drop in ion flux to the specimen and the production of large ion sheaths if the plasma production mechanism is not strong enough to cope with the ion loss.

Depending on the plasma source type, there are various methods to increase plasma production. For example plasma produced by a filament or RF discharge, the density can be enhanced by confining electrons in a magnetic multipole "bucket" geometry [9, 10]. High-density plasmas require a high concentration of energy and as a result they tend to be non-uniform [11].

In [12] we reported an original method to enhance periodically the plasma production in RF-driven plasma source for surface treatment of materials by ion implantation. The method consisted in applying supplementary very short positive high voltage pulsed discharges on a separate electrode synchronized with negative pulses applied on the target for ion implantation. By this method RF plasma density was increased with an order of magnitude shortly before applying accelerating pulses on the target. The advantages of this new method were revealed by nitrogen implanted tests on copper and brass samples [12].

The work presented below aims to demonstrate that our plasma enhancement method works for metal ion implantation on non-metallic surfaces, too, and to show its benefits compared to a classical method.

2. EXPERIMENTAL SET-UP

The plasma source that uses the enhancement of plasma density, as described in [12], consists of a chamber divided in two volumes by a grounded grid (Fig.1). The sample placed on the target electrode and biased at high negative voltages is processed by immersion the RF plasma in the large part of the chamber. The small volume, delimited by the grid, is reserved to positive high voltage discharges, which modulate RF plasma by injection of charged and metastable atoms. The role of metastable atoms in pulsed discharges was extensively studied in [13–19].

Capacitive coupled RF plasma was continuously and asymmetrically generated in quasi-static argon buffer gas at low pressure (few Pa), using one RF electrode 3 cm in diameter made of copper, which was driven by a 13.56 MHz RF generator connected through a tuned matching network.

High voltage (HV) pulsed discharges are periodically generated in the smallest part of the chamber by applying very short (~100 ns) high voltage (6 kV) positive pulses on a separate electrode at a repetition rate of about 30 Hz. The HV generator uses a very robust and reliable switching device, namely, rotary spark-gap, described in detail in [20].

Negative pulse generator is synchronized with the positive pulse generator using a pulse transformer, whose primary winding is inserted in the positive pulses generator circuit. Figure 2 presents the negative pulsed voltage measured on the target synchronized with the positive pulsed discharges.

The transient phase of RF plasma can be qualitatively observed on voltage time evolution measured on the target electrode through a HV probe (Fig. 3).

The processed surfaces were analysed by X-Ray Photoelectron Spectroscopy (XPS). A VG-ESCA Mk-II installation was used, with base pressure in 10^{-9} mbar range in the analysis chamber. The excitation energy used was 1486.7 eV (Al K_{α}), without further monochromating. The estimated electron inelastic mean free path for electrons with binding energies of ~ 100 eV (such as Si 2p, Cu 2p-2s etc.) is about 1.6 nm [21]. A Specs electron flood gun operating at 3 V acceleration voltage and 0.3 mA electron current was used in order to ensure sample neutralization. These values were chosen after performing several calibration tests on Au 4f_{7/2} level on Au foils (83.8 eV) [22] and on the C 1s originating from adventitious contamination of the sample surface (284.8 eV). The data were analyzed by using custom made packages developed under the Igor Pro platform. The concentrations were determined from integral line intensities by using the Wagner atomic sensitivity factors [23]. The NIST XPS database (<http://srdata.nist.gov/xps/>) was constantly checked together with other databases, such as Refs. [24, 25], in order to assess the identified chemical shifts.

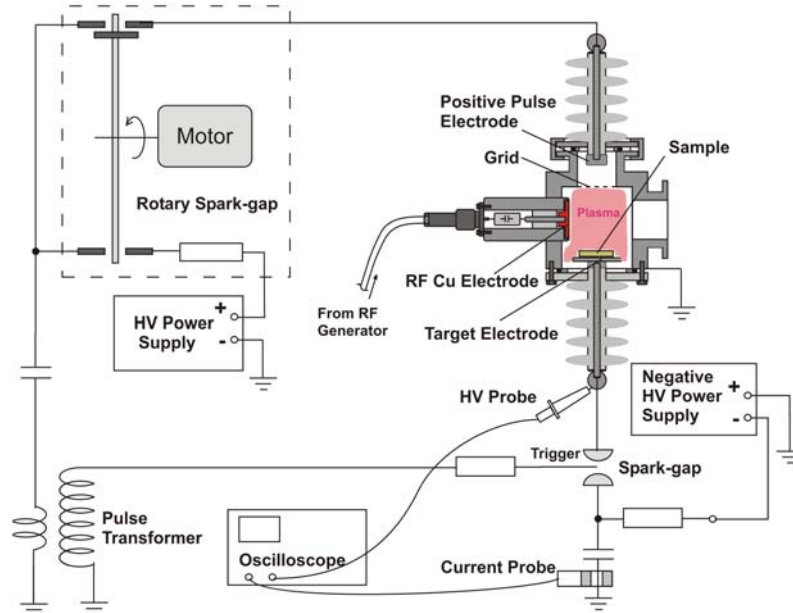


Fig. 1 – Experimental set-up.

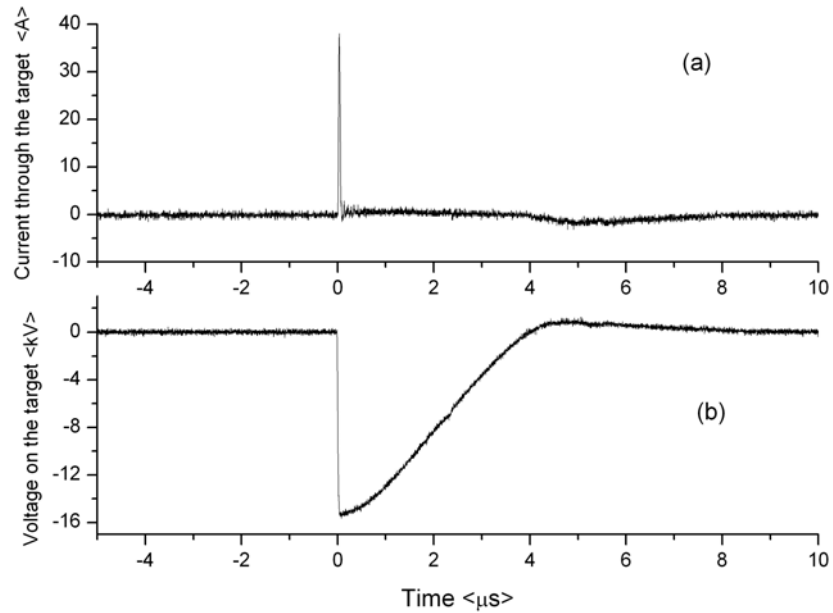


Fig. 2 – Negative pulse on the target synchronized with positive HV discharge.

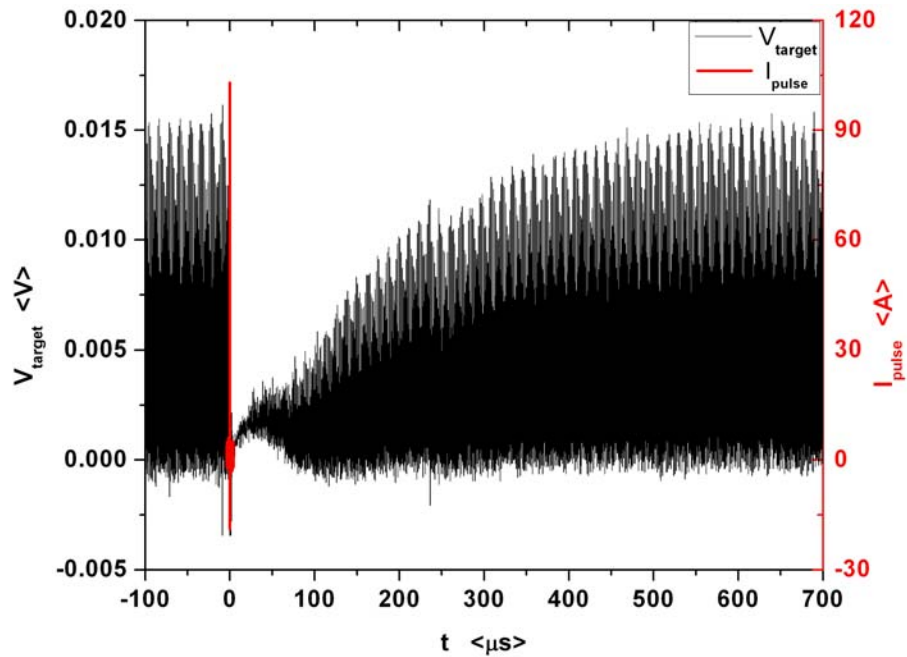


Fig. 3 – RF voltage signal measured on the target electrode (V_{target}) and current signal (I_{pulse}) of positive pulsed discharge (in red).

3. RESULTS AND DISCUSSIONS

In order to test the new enhanced plasma source for metal ion implantation and deposition, the nitrogen plasma used in previous tests [12] was replaced with metal vapour plasma obtained by sputtering the copper RF electrode with Ar ions.

The tests consisted in processing glass surfaces with Cu ions by implantation and deposition using our ion source in which RF plasma is strongly enhanced in the wake of the very short HV positive pulses. The glass samples were compared with those processed by two conventional methods: (i) classic RF plasma deposition; (ii) classic RF plasma ion implantation and deposition.

Experimental conditions can be summarised as following: Ar gas pressure 2.5 Pa; RF power 30 W; positive pulses voltage 6 kV; negative pulses voltage 15–16 kV; pulse repetition rate 30–40 Hz; processing time 10 minutes.

The processed samples were analyzed by X-Ray Photoelectrons Spectroscopy (XPS). The overview XPS spectra of surfaces (few nm depths) of the three processed glass samples are presented in Fig. 4.

Analysing the spectra we observe that the copper amount at surface is largest in the case of simple RF plasma deposition, while the smallest amount of copper is obtained at the surface of sample treated by implantation in RF + pulse regime. One can easily observe that apart the Cu (Cu 3p, Cu 3s, Cu 2p), all the samples contain impurities like carbon and oxygen, which are specific for samples prepared in other conditions than *in situ* ultra-vacuum (10^{-10} mbar).

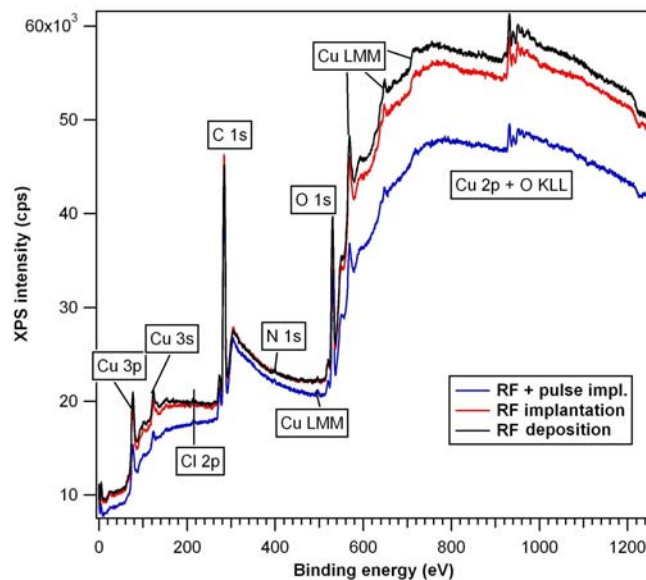


Fig. 4 – Overview XPS spectra of glass sample surfaces processed by RF deposition, RF implantation and RF + pulse implantation.

The detailed regions of Cu 2p (Fig. 5) show the presence of the doublet spin-orbit (Cu 2p_{3/2} and 2p_{1/2}). However, here, each level from the doublet presents a supplementary split, due to the copper from the metallic layer and the oxidized copper from the surface [24, 25].

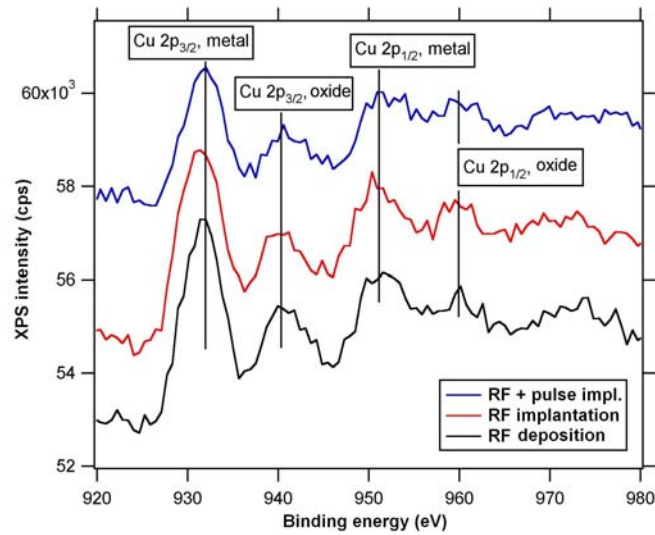


Fig. 5 – Deep levels region, Cu 2p.

It is remarkable to observe that the lowest contamination of the Cu layer is obtained by implantation and deposition in RF + pulse discharge configuration. Figure 6 presents low binding energy region, Cu 2p si 2s, Si 2p si 2s, and O 2s.

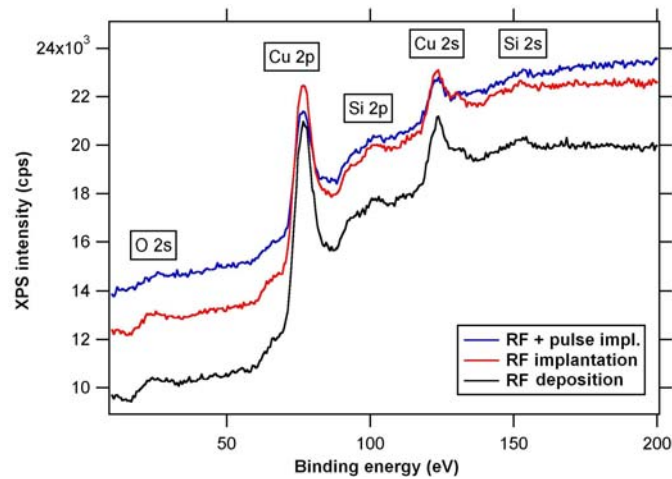


Fig. 6 – Low binding energy region (Cu 3p, Cu 3s, Si 2p, Si 3s).

The line O 2s intensities confirm that the degree of contamination of the sample processed in RF + pulse is the lowest.

Lines of Si, which is one of the main components of the substrate, are strongly attenuated indicating that the Cu layer is thicker than analysing depth possibility of the XPS method.

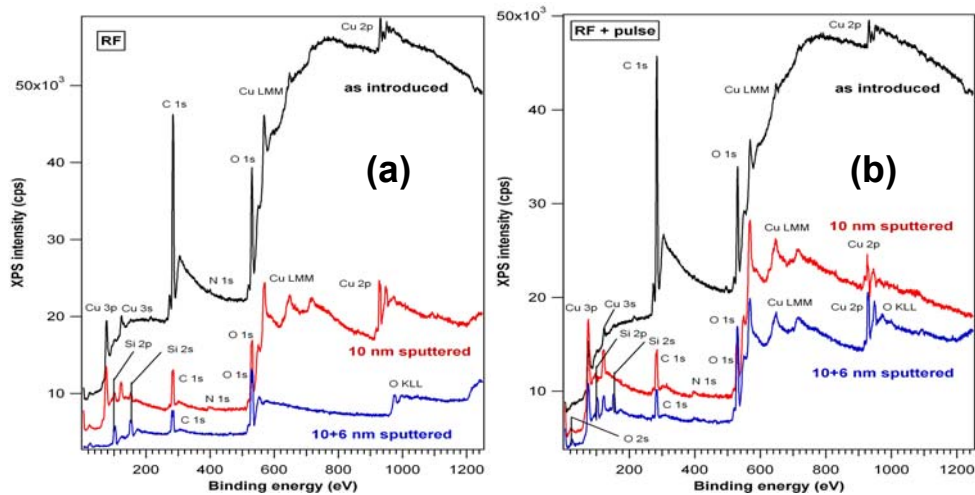


Fig. 7 – XPS spectra of Cu layers on glass substrate at various depths obtained by ion sputtering: a) sample implanted in classical RF plasma; b) sample implanted by immersion in transient plasma of RF + pulse discharge.

Although we found a larger amount of Cu at the sample surface obtained by implantation and deposition in RF plasma than at the sample surface implanted by immersion in RF + pulse plasma, it is important to measure the Cu depth profile, because we expect that Cu diffuses in glass substrate.

In order to assess Cu depth profile, the samples were sputtered with Ar ions (inside XPS device). Figure 7 presents XPS spectra at different depths in samples treated by two methods, RF plasma ion implantation and deposition, and RF + pulse plasma ion implantation and deposition, respectively.

As we have already observed, there is a larger amount of copper at the non-sputtered surface of the sample implanted in RF plasma than in RF + pulse plasma, but there is no doubt that, at 16 nm depth the copper lines totally disappear in RF case, while Cu lines are still well visible in the case of RF + pulse. On the other hand, Si lines, the main component of the substrate, start to be visible from 10 nm depth, and significantly increases at 16 nm, revealing that at this depth we are in the glass substrate. So, the copper ions penetrate deeper in the substrate when the samples are treated by our method.

4. CONCLUSIONS

The metal layer deposited and ion implanted by immersion in classical RF plasma is thicker but less compact, containing a very small amount of metal at the interface with substrate.

When the substrate is implanted and deposited in RF + pulse plasma, the metal layer is thinner but more compact and a large amount of implanted ions can be found in the substrate. Another benefit of this method is that the metallic layers are less contaminated.

Therefore, the synchronous enhancement of RF plasma using supplementary HV pulses was proved to be a valuable method to increase the efficiency of metal ion implantation on non-metallic surfaces.

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