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## Differences between thin films deposition systems in the production transition metal nitride

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**Abstract.** The progress in vacuum technology have enabled the development of advanced coatings processes such as plasma assisted systems, which can produce thin films of different composition and optimum properties, that cannot be collected for the same material. The techniques of Pulsed Arc, Ionic Implantation and Sputtering have differences to produce coatings. Currently, AuN films have been grown by different techniques such as ion implantation, Reactive Ion Sputtering and Pulsed Arc, which have differences in the grown of the film. Siller 2002 reported a binding energy of 396.6 eV to N1s narrow spectrum as the first direct observation of a gold nitride. In this work, AuN thin films were grown in a system Plasma-Assisted Physical Vapor Deposition by pulsed arc technique. A N1s spectra was obtained with binding energies of 398.1, which by means of the differences between the techniques of ion implantation, sputtering and pulsed arc is concluded have been assigned to gold nitride species.

### 1. Introduction

The physics of the electrical discharges study the process of the generation, maintenance and transport of electrical currents in an ionized gas. Between 1950 -1960 it started the real development of new plasma technologies in relation with materials process and thin films [1]. I. Langmuir in early 1920 introducing the word "Plasma" to describe the ionized gas, for through of yours studies on the valve to allow the pass of high currents. He defined this term as a gas of neutral and charged particles (quasi-neutrals) that present collective behavior. The "Plasma" is related with the possibility of "give form" using electrical and magnetic fields, thus avoiding the need of a container as the fluids, liquids or gases. The plasmas are generated through high energetic process, as are the electric discharges in gases or the heating to high temperatures of a gas [1]. The luminescence discharges (electrical discharge type) developed in ionized gas are produced through an electrical discharge to low pressure and are used to thin films production, because in this zone is produced a high of ion bombardment on cathode and the relation current-voltage is almost lineal [2]. The material treatment from plasmas generated for electrical discharges are classified in: i) deposited thin films to low and atmospheric pressure (< 10 - 20 Torr); ii) process of plasma attacks to low pressure (< 0.05 Torr) and different types of superficial treatments to atmospheric pressures; iii) use plasma as ion source, that are used



subsequently in the surface treatment. This paper is a recollection of the different techniques used to produce AuN (Transition Metallic Nitride), Ionic Implantation, Sputtering Reactive and Arc Pulsed.

The differences in the plasma generation to produce a thin film influence in the nitride species obtained, which in turn have its own chemical state, physical and mechanics properties [3]. N1s spectra narrow were obtained for the X-Ray Photoelectron Spectroscopy (XPS) to AuN samples growth for arc pulsed technique and compared with N1s narrow spectrum obtained for Siller to nitride species of gold for Sputtering reactive and Implantation Ionic techniques [4, 5], and ends with analysis on the influence of the techniques in the production of nitrides species of gold.

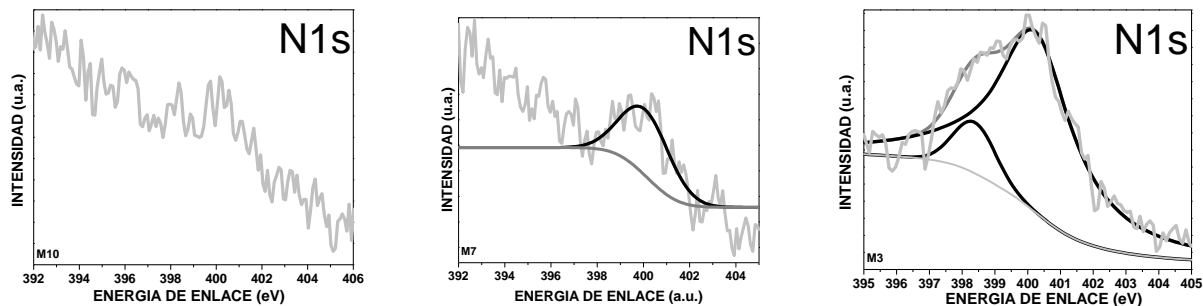
## 2. Experimental

AuN thin films growth for arc pulsed technique were obtained in the Plasma Physics Laboratory (LAFIP) of the Universidad Nacional de Colombia [6]. This technique was used due to the high ionization grade in the moment of the discharge, which would lead to obtain species to more high binding energies of the N1s Narrow spectrum that showed Siller with Ionic Implantation and Sputtering Reactive. The arc used in this system is of "Cathode Arc", in which two electrodes are face to face, the position of cathode is gold and the anode is stainless steel. The process to obtaining the thin films, the chamber was evacuated to a vacuum of about  $10^{-7}$  mbar, the capacitor bank was charged at 200 V power, alongside the substrate was heated to a temperature of  $140^{\circ}$  C. nitride pressure. The nitrogen pressure in the discharge time for each sample was varied in a range of 2.0 to 8.0 mbar; 3 discharges were performed with the same parameters and then nitrogen was introduced until a pressure of  $10^2$  mbar, to hold the films deposited for 3 hr. For comparison with the other techniques, only used M3 (3.5 mbar), which introduced species nitride gold. To obtain spectra N1s narrow a His 165 and AXIS ULTRA, with resolution of 0.35 eV was used. Lorentzianas-Gaussian functions and a Shirley background were used to obtain the binding energies.

## 3. Results and discussion

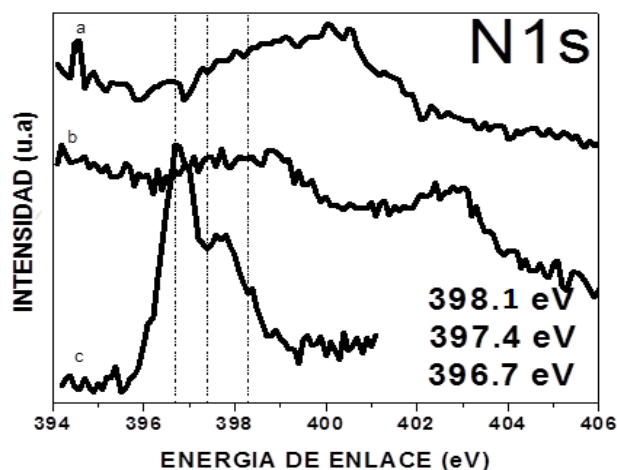
In the figure 1 is showed the N1s narrow spectrum to M3, M7 and M10 samples obtained for arc pulsed technique. The absence of nitrogen in M10 could be attributed to the decreased by the mean free path of the particles within the plasma since this was produced at a pressure 7.0 mbar. Para M10 no fue posible la deconvolución del espectro angosto N1s, debido a la baja intensidad del pico (indicativo de baja concentración de N). En M3 se encontró hibridación del espectro angosto N1s en el rango de  $396.0$  a  $398.0 \pm 0.2$  eV ( $398.1 \pm 0.2$  eV), the which have been attributed to species nitrogen with transition metals [5, 7, 8]. The highest peaks frequently appear in the XPS binding energy analysis to samples grown in plasma assisted systems, due to the vacuum that is used at the time of discharge ( $\sim 1$  mbar) and are attributed to the formation of carbo-nitrides and oxy-nitrides [9, 10]. N1s narrow spectra obtained for samples grown by ion implantation, reported  $396.7 \pm 0.1$  eV and  $397.7 \pm 0.1$  eV binding energies as gold nitrated species [4], further observed that the heat treatment changes the narrow spectral line N1s spectrum, which has been attributed to differences in the thermal stability of the nitride species. For samples produced by sputtering were reported  $397.5 \pm 0.1$  and  $398.9 \pm 0.1$  eV binding energies, the low energy was attributed to chemical bonds between gold and nitrogen [5] (also observed by ion implantation). The highest energy peak was previously assigned to oxy-nitride bonded with gold [8, 11]. The difference between the three binding energies in the N1s narrow spectrum can be explained by means of the acceleration of the particles arriving at the substrate; the Ion Implantation have an acceleration few eV [1], the Sputtering have between 10 to 40 eV [1], and the Pulsed Arc technique have acceleration from 50 to 150 eV [12, 13, 14], this difference is influenced by the properties of the plasma produced [1, 15]. The high average energy of the particles (Te) in nonthermal plasmas (usually used in these systems), makes it possible in the collision processes including the gas atoms and molecules are activated by high energy chemical reactions leading to the formation of free radicals in physicochemical environments where the temperature of neutral species (Tg) is reduced 300-1000 K. In this collisions, is produced too ionized species and, above all, to the formation of highly excited atoms and molecules. In the early stages of thin film

growth occur a series of steps at the microscopic level, with its own complex mechanism: arrival of the surface atoms (arrival energy of the atoms), subsequent adsorption and surface diffusion (growth rate), nucleation, formation of nuclei and growth of a continuous layer (pressure and temperature). The set of all these stages largely determines the structure and morphology of the deposited layer and therefore its physicochemical properties [16]. The atoms that reach the surface with high energy (so that they have more time to thermalization with the surface) correspond to a higher crystalline structure. Conversely, when the arrival energy of the atoms is small the length of diffusion is smaller, and the positions of adsorption would reach lower binding energy.



**Figure 1.** N1s narrow Spectrum, to Samples growth for Arc Pulsed.

Once the islands coalesce and form a continuous layer of material deposited on the substrate, the atoms arrive at the surface and are incorporated to microstructure of the coating, through process of the superficial diffusion and absorption (As in the initial stages); also is show processes like diffusion adatoms along grain joints, to fill the pores and channels which are formed in the film growth; the latter two processes generally appear at higher temperatures and are thermally activated [17].



**Figure 2.** N1s Narrow Spectrum Superposition a) Pulsed Arc, b) Sputtering [6] y c) Ion Implantation [5].

In the spectra obtained for Transition Metallic Nitride, there was an increase of the binding energies (BE), in relation with the system used to growth thin film (see figure 2). The sample of Ion Implantation 396.6 eV, Sputtering 397.5 eV and Pulsed Arc 398.1 eV, which lead to think that the plasma produced in each of this technique, has the appearance of different gold nitride species. The chemical change of a material is directly related to the total charge of the atom (if the load is reduced, increases binding energy). Leading to: i) Increased number of substituents ii) Electronegativity of substituent iii) formal oxidation state. Usually chemical changes are considered as initial state effects.

Chemical changes of  $Ti2p_{1/2}$  and  $2p_{3/2}$  change to Ti and  $T^{4+}$ . The charge then would change  $Ti \rightarrow Ti^{4+}$ , then the 2p orbitals is relax to higher binding energies. Very similarly a change of this type is observed in Transition Metallic Nitride.

#### 4. Conclusions

We compared three production systems Transition metal nitrides (Ion Implantation, Sputtering Reactive and Pulsed Arc) and it was observed that the acceleration of the particles when reaching the surface to have remarkable impact on the production of different species nitride.

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