Nitrogen Atoms into Ru Phases

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Abstract

Nobel Transition Metals may be good candidates for catalysts, it would entail to think that nitride noble metals could improve this property, so it is really good study this materials type. A reactive Magnetron Sputtering was used to obtain nitrogen into Ru phases. It variations of the Ar/N₂ ratio at moment discharge were used to vary the nitrogen concentration at surface thin film. A 397.4 ± 0.3 eV, 398.3 ± 0.3 eV, and 398.8 ± 0.3 eV binding energies were obtained since N1s narrow spectrums and it assigned to nitride hybridized with transition metal (RuN), Oxy/Carbide nitrides, respectively. A Grazing Incidence through a X-Ray Diffraction analyses were performed and determined showing the coexistence of the RuN face centered cubic and Ru hexagonal compact packed phases.

Keywords: Ruthenium Nitride, Grazing Incidence, N1s Narrow Spectrum

1 Introduction

In the last years, researching about noble metal (Au, Pt, Ru among others) nitrides is growing, because those metals were not thinking to obtain it [1-3]. Introduce nitrogen into metal would improve mechanical (hardness), electrical, magnetic and optics properties and it would open it a big possibility in industrial applications [4-6]; for example, RuN has been proposed in microelectronic compound and electrodynamics capacitors [7, 8]. Catarruza and Laik has produced RuN thin films with low nitrogen amount through thermic treatments in a Magnetron Sputtering system [9, 10], because it requires large energy densities for their formation (high pressures and temperatures) and they observed that high temperature the nitrogen evaporated, and crystalline structure reorganized its in metallic hexagonal close-packed ruthenium.
In this work, nitrogen atoms into Ru phases were obtained through Sputtering Magnetron system. RuN species through N1s Narrows spectrum were visualities and a coexistence Ru and RuN phases were observed by means the grazing incidence analysis (X-Ray Diffraction).

2 Experimental Set up

A Sputtering system of the AJA International were used to obtain RuN thin films. 5 Pa pressure, a 200 °C temperature substrate and 85 watts power was used to every sample. Only it was changed the Ar/N₂ relation at moment discharge (see table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
<th>M6</th>
<th>M7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar/N₂</td>
<td>100/0</td>
<td>98/2</td>
<td>95/5</td>
<td>90/10</td>
<td>85/15</td>
<td>80/20</td>
<td>60/40</td>
</tr>
</tbody>
</table>

A ruthenium target of 99.999% purity and Silice were used as cathode and anode, respectively. An XPS (XPS Specs) with Al Kα (1486.6 eV photoelectron energy) was used to obtain the high- and low-resolution spectra. Wide spectrum was acquired between 1200 and 10 eV, then, high-resolution N1s and Ru3d spectra with steps of 0.03 eV were obtained. Casa XPS was employed to develop deconvolutions with Gaussian-Lorentzian functions. The calibration of the spectra was carried out by using the Ru3d (280.5 eV), because the C1s peak is overlap with Ru3d peak. The X-ray diffraction (PANalytical instrument) with a Cu anode (Kα = 1.5406 Å). Parallel beam geometry was acquired with a voltage of 40 kV and a current of 40 mA in the tube. Grazing incidence to 0.2, 0.5, 1.0, 1.5, 2.0 and 2.5 were collected to observe the RuN phases.

3 Results and Discussion

![Figure 1. N1s Narrow Spectrum to M2, M3, M4, M5, M6 and M7 samples.](image-url)
N1s narrow spectrum to M2, M3, M4, M5, M6 and M7 are showed in the figure 1. For M1 is not shown because it did not have nitrogen. Those were deconvoluted with Gaussian and Lorentzian functions and it was possible observe the presence of two peaks about 398.9 eV and 397.5 eV corresponding to oxynitrides or carbonitrides and transition metal nitrides, respectively [11].

**Figure 2. Grazing Incidence**

The oxy/carbonitrides are common in thin films obtain for those system, because the vacuum is low, besides sample has contact with environment because the system and XPS equipment are not connected. Energies about 396 eV to 398 eV are known as hybridizations of nitrogen with transition metals, in this case RuN.
In the sample M5 was observed an additionally energies around 398.5eV. It was found in the limit of hybridization with metal and oxy/carbon nitrides, when compared with diffraction pattern, this sample has the best the amount of RuN phases. It would entail us to say that nitrogen has different hybridizations with Ruthenium metal [12-14].

Diffraction patterns to M2, M3, M4, M5, M6 and M7 are shown in the figure 2. Those patterns were possible to observer the characteristics peaks of Ru Hexagonal Compact Packed (HCP) crystalline structure; although in some samples appear peaks between 35° - 45° angles characteristic to RuN (FCC) crystalline structure [9, 13]. A grazing incidence analysis were made to observe if the peaks correspond to RuN phases. It is possible note, that the peak remains in every sample to every grazing, only in the 2.5 incidence to M3 appears only substrate peaks, this could be because the sample is very thin and the X-ray can cross it.

![Diffraction Patterns](image)

**Figure 3. Grazing Incidence to 36 – 50 (2 Theta - Grade)**

In figure 3 a zoom was made between 35° to 50° angles and the diffraction pattern were normalized to observe the peaks. This is shown that to M5, M6 and M7 have RuN phases, because the peaks are close to 40°, as others research have reported [9]. M5 sample has more amount RuN phases with respect to the other samples because the RuN peaks is predominant at this, which can be verified with XPS analysis.

### 4 Conclusions

Grazing incidence and N1s narrow spectrum analysis were presented to explain the coexistence of RuN phases in Ru films. The discharges made to nitrogen relations above to 15 % with respect Argon, it produced RuN thin films.
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