On the synthesis and thermal stability of RuN, an uncommon nitride

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INTRODUCTION

Ruthenium nitride (RuN) is a compound that under ambient conditions presents a positive enthalpy of formation. Recently [1] we synthesized RuN thin films in the zinc-blende structure by radiofrequency magnetron sputtering. We found that a fundamental parameter for the synthesis of this compound is the temperature of the growing film: in film deposited on substrates intentionally heated at 100 °C and above we did not detect any presence of nitrogen. At source powers as low as 60 W, the N/Ru atomic ratio is lower than unity, because of the increase in the substrate temperature due both to radiant heating from the source and direct energy deposition by particles striking the substrate during the film growth. Moreover, we studied the electrochemical behavior of the synthesized layers [2] and found that under hydrogen evolution conditions, the films showed relevant catalytic properties, comparable with Pt, Pd and Ru/Ir derivatives. Promising results were obtained by B. Laik et al. [3] who investigated the RuN electrochemical behavior as negative electrode for Li-ion microbatteries.

In spite of the detailed investigation on the influence of several synthesis parameters reported in our previous paper [1], many open questions remained. In the first part of this paper we disclose relevant aspects of the effect of the direct energy deposition by particles striking the substrates during the film growth. This has been accomplished by modifying the configuration of the source magnets to switch from the unbalanced magnetron sputtering (UBMS) to the balanced magnetron sputtering (BMS). In the second part we report on the study of the thermal stability of the synthesized compound subjected to isochronal annealing either in ultra-high-vacuum (UHV) and in air. Results of a further electrochemical characterization are also reported.

EXPERIMENTAL

The sputtering apparatus has been described in detail in our previous work [1]. The base pressure in the chamber was in the range 1±2×10\(^{-5}\) Pa. Depositions were performed using mixtures of Ar (99.9995 %) and N\(_2\) (99.9999 %) at partial pressures of 0.25 (±0.02) Pa and 0.35 (±0.02) Pa, respectively. The target was a 2 inches diameter, 0.25 inches thick, Ru (99.95 %) metallic disk. The rf-power to the target was varied in the 50-150 W range. The configuration of the source magnets was set to obtain the balanced magnetron sputtering (BMS) configurations [4]. Syntheses were performed at room temperature (without intentional heating of the substrate holder). For the annealing studies, films were synthesized onto 7.5×2.5 cm\(^2\), 1 mm thick, silica sheets at the source power of 50 W. Small pieces (about 1x1 cm\(^2\)) were then cut from these and treated at the selected temperatures. Thermal treatments were performed in the temperature range 200°C-350°C in ultra-high vacuum (UHV) in the range 2±4×10\(^{-5}\) Pa, and in air. After a heating ramp of about 1 hour (heating was rapid at the beginning and slow as the chosen temperature is approached), the temperature was maintained fixed (within ±5 °C) at the selected value for 1 hour, then the power was switched-off and samples allowed to cool in their environment.

Samples were characterized by Rutherford backscattering spectrometry (RBS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS); details are reported in reference [1].

RESULTS AND DISCUSSION

Balanced magnetron sputtering synthesis

In our previous work [1] we synthesized RuN layers in the UBMS configuration. Such a configuration enables high deposition rates, but also causes a substantial ion bombardment of the substrate, because the plasma is not strongly confined to the target region, but it is allowed to flow out towards the substrate. On the contrary, in the BMS configuration used in this work the plasma is strongly confined to the target region. In this latter configuration deposition rates are lower, but the ion bombardment of the substrate is highly reduced [4]. The composition of the layers has been obtained by fitting the experimental RBS spectra (not reported) with spectra synthesized by the RUMP code [5]. Results are reported in Table 1, where R is the measured N/Ru atomic ratio (±0.1) and D is the film growth rate in units of 10\(^{13}\) (atoms/cm\(^2\))/s of Ru. The uncertainty on D values is about 5%. All R and D values reported hereafter are affected by the same uncertainties.

Table 1. Measured values of the N/Ru atomic ratio (R) and of the film growth rate (D) (in units of 10\(^{13}\) (atoms/cm\(^2\))/s of Ru), as a function of the power supplied to the ruthenium source (W\(_{Ru}\)).

<table>
<thead>
<tr>
<th>W(_{Ru}) (W)</th>
<th>50</th>
<th>75</th>
<th>90</th>
<th>100</th>
<th>120</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>D</td>
<td>6.0</td>
<td>9.7</td>
<td>11.1</td>
<td>13.1</td>
<td>17.5</td>
<td>22.8</td>
</tr>
</tbody>
</table>
If we consider that, for the UBMS configuration the value \( R=1 \) could be obtained at powers not exceeding 50 W (with a \( D \) value of \( 7.3 \times 10^{13} \) atoms/cm\(^2\)/s of Ru) [1], the effect of the reduced substrate bombardment in the BMS configuration is evident: the maximum power that can be used keeping \( R=1 \) is nearly twice as much, with a large increase of the deposition rate.

We believe that the reduced substrate bombardment in the BMS configuration results in a reduced Ru-N bond breaking caused by direct interactions between particles impinging the substrate surface and the already formed RuN; moreover, the lower ion current results in a reduced heating of the substrate, thus favoring the formation of Ru-N bonds because of the lower desorption rate of the already condensed species.

**Thermal treatments**

In figures 1 and 2 we report the N/Ru and O/Ru atomic ratios, obtained by RBS analysis, as a function of the annealing temperature in UHV and in air, respectively.

In UHV a nitrogen loss begins to occur at a temperature between 230 °C and 250 °C. Above this, the loss steeply increases. As demonstrated by the XRD analysis (not shown), this loss of nitrogen results in the conversion of RuN to metallic ruthenium. The small increase in oxygen content at temperatures above 250 °C is most probably related to oxygen uptake occurring when samples are exposed to air.

In air RuN decomposes at a temperature lower than that observed for the UHV annealing, but at much lower rate. This evidence, and the oxygen uptake, could be related to chemical interactions between formed RuN and species present in the environment, leading to the formation of ruthenium oxides or oxynitrides. On these results, and on XRD and XPS measurements (not reported) the most reliable picture of the surface evolution of the deposited RuN film during the annealing in air can be described as follows: up to about 250 °C chemical reactions between RuN and species present in the environment occur at the surface, with the formation of oxynitride and hydroxide ruthenium compounds. This surface compound layer slows down the nitrogen outdiffusion, thus hindering a fast decomposition of RuN. On the other hand, this layer is partially permeable to molecular oxygen which interacts with ruthenium to form RuO\(_2\) if the temperature is high enough (above 250 °C). Metallic ruthenium is detected at about 300 °C and this can be due to the fact that not enough oxygen crosses the surface compound layer to completely oxidize the ruthenium atoms made available after the nitrogen outdiffusion.

**Electrochemical characterization**

Recently [6] we investigated the electrochemical behavior of our films and put into evidenced that RuN tends to adsorb hydrogen when subjected to a cathodic polarization. Plausibly, the process takes place within the hydrated region of the film, through the reduction of Ru(III) to Ru(II) and with the formation of RuNH. Once formed, the latter is able to catalyze efficiently the process of hydrogen evolution, as commented in our previous work [2]. The reversible formation of RuNH allows accounting for the large pseudo-capacitance of RuN, which suggests that the material can be also of interest for supercapacitors in aqueous alkaline media.

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