Quintero JH, Marino A, Siller L, Restrepo-Parra E, Caro-Lopera FJ. Rocking curves of gold nitride species prepared by arc pulsed-physical assisted plasma vapour deposition. *Surface and Coatings Technology* (2016)

DOI: [http://dx.doi.org/10.1016/j.surfcoat.2016.11.081](http://dx.doi.org/10.1016/j.surfcoat.2016.11.081)

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DOI link to article:

http://dx.doi.org/10.1016/j.surfcoat.2016.11.081

Date deposited:

25/11/2016

Embargo release date:

24 November 2017

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Accepted Manuscript

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PII: S0257-8972(16)31215-4
DOI: doi: 10.1016/j.surfcoat.2016.11.081
Reference: SCT 21827

To appear in: Surface & Coatings Technology

Received date: 19 September 2016
Revised date: 21 November 2016
Accepted date: 22 November 2016

Please cite this article as: J.H. Quintero, A. Mariño, L. Šiller, E. Restrepo-Parra, F.J. Caro-Lopera, Rocking curves of gold nitride species prepared by arc pulsed - physical assisted plasma vapor deposition, Surface & Coatings Technology (2016), doi: 10.1016/j.surfcoat.2016.11.081

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Rocking Curves of Gold Nitride Species Prepared by Arc Pulsed - Physical Assisted Plasma Vapor Deposition

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4. Laboratorio de Física del Plasma, Universidad Nacional de Colombia, Colombia

Abstract

Gold nitride is important for potential applications, such as, to replace metallic gold in electronics, coatings, jewelry and micro-engineering. However, the experimental determination of crystalline structure is still controversial due to difficulties in the synthesis (it is difficult to obtain a sufficient amount). In this work gold nitride species are obtained at the 304 stainless steel substrates by using an arc pulsed - physical assisted plasma vapor deposition system. The pressure of nitrogen at the discharge time was varied between 3.5 at 8.0 mbar to increase the amount of gold nitride species in the sample. By X-ray diffraction, changes in the texture coefficient of (111) to (200) planes are observed, and increase of the micro strain, asymmetries and widening of the rocking curves shown. By the X-ray photoemission spectroscopy, the N 1s core levels observed at binding energies of 398.1 eV and 398.3 eV, are attributed to formation of gold nitride species.
The rocking curves of gold nitride films are modeled by using a recent theory of shape and influential curves. From this modelling, a cubic crystalline structure of the gold nitride is proposed.

Key words: Gold Nitride, Rocking Curve, Influential Curves, Assymetries.

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1. Introduction

Today, the research into synthesis of new materials is very important because of the necessity to improve our environment by new applications. Production of nitrides and carbides of the noble metals, with improved physical or chemical properties such as greater hardness, thermal stability, higher melting point and higher electrical conductivity which have numerous applications in the industry is of significant interest to the current research [1]. In the last decades, noble metals that belong to the platinum group (Pt, Au, Ir, Os, Ru among others) have attracted attention, mainly for the production of PtN, AuN, IrN and RuN, to increase their amount and fundamentally to determine their activation barriers [2-6].

The gold nitride thin films are of interest to replace metallic gold in electronics, coatings, jewelry and micro-engineering [7-12]. The gold nitride films have been obtained by ion implantation (with a binding energy of $396.7 \pm 0.2 \text{ eV}$) [2, 3], laser ablation (no reported) [6, 7], arc pulsed (with a binding energy of $398.1 \pm 0.2 \text{ eV}$) [13] and reactive ion sputtering (with a binding energy of $397.7 \pm 0.2 \text{ eV}$) [11, 14, 15]. The difference in these reported binding energies are likely to be due to different accelerations of
charged nitrogen ions arriving at the gold substrate or due to different nitrogen plasma densities at the surface of the target. This is a likely reason why using arc pulsed system produces more amount of gold nitride species [16].

The binding energies of gold nitride species were determined by X-ray photoelectron spectroscopy (XPS) studies [2, 3, 14]. Additionally, there is indication of presence of interstitial nitrogen in the Au-face-center-cubic (fcc) structure [15]. Our most recent study of the rocking curves obtained by x-ray diffraction (XRD) on gold nitride synthesised by arc pulsed - physical assisted plasma vapor deposition (AP-PAPVD) which showed that as the nitrogen atoms are introduced into the Au-fcc structure it was not possible to detect the difference in the Au diffraction patterns [17, 18]. For this reason it is still necessary to perform further studies related to modification of those patterns. Furthermore, analysis of the compositional, structural and morphological properties upon the influence of deposition parameters during AP-PAPVD, such as finding the optimal nitrogen flow rate, is still required because the amount of species of gold nitride in our previous studies was very low. On the other side, computational studies by the density functional theory (DFT) suggest possible gold nitride crystal phases such as triclinic, trigonal, rock salt, zinc blende, wurtzite and fluorite [3, 19-23]. In this work we report: i) a changes in the texture coefficient of the Au diffraction patterns ii) a strong widening of the rocking curves (much larger to previously reported in reference [18]) iii) improved amount of gold nitride species in the gold thin films and iv) modeling of the rocking curves in order to study the difference between the curves of Au species, Au and N species and AuN species.

2. Experimental set-up
Gold nitride species are grown in a noncommercial AP-PAPVD system (at Universidad Nacional de Colombia, Colombia) on substrates of 304 stainless steel. The system consists of a cylindrical stainless steel reactor (26 cm long with 30 cm in diameter) with two electrodes (cathode and anode) confronted to 4 mm of distance. The anode is a circular gold rod (25 mm diameter, 1 mm thick and 99.999 % purity - Vortex Company) while the cathode is the substrate (1.3 cm diameter, 2 mm thick). A mechanical and a turbo molecular pump are used to achieve a vacuum of $1 \times 10^{-7}$ mbar. The discharges are conducted in an atmosphere of pure nitrogen (99.999 % Molar - AGA) and the pressure at the time of discharge was varied between 2.0 and 8.0 mbar (in 0.5 mbar steps). The samples grown at 2.0, 2.5 and 3.0 mbar have the same properties as published previously in reference [18]. Sample grown at pressure of 4.5 mbar showed the same results as sample grown at 5.0 mbar and 8.0 mbar, while the samples grown at pressures of 5.5 mbar, 6.0 mbar and 6.5 mbar showed the same results as samples grown at 7.0 mbar and 7.5 mbar, so they are not all separately presented in this work. The growth discharge conditions for gold nitride films grown on 304 stainless steel substrates are given in Table 1.

**Table 1.** The growth discharge conditions for gold nitride thin film grown on 304 stainless steel substrates.

<table>
<thead>
<tr>
<th>SAMPLES</th>
<th>M3</th>
<th>M4</th>
<th>M6</th>
<th>M10</th>
<th>M11</th>
<th>M14</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRESSURE (mbar)</td>
<td>3.5</td>
<td>4.0</td>
<td>5.0</td>
<td>7.0</td>
<td>7.5</td>
<td>8.0</td>
</tr>
<tr>
<td>ARCS NUMBER</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAS</td>
<td>Nitrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VOLTAGE (Volts)</td>
<td>200</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEMPERATURE (°C)</td>
<td>140</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The XPS analysis was carried out by an X-Ray Photoemission Spectrometer (Kartos Axis Ultra 165 at Newcastle University, UK) equipped with a monochromatic AlKα X-ray source. Survey spectra and core level regions are obtained with an energy resolution of 0.1 eV. The pass energy of the hemispherical analyzer for core levels was 20 eV and for survey spectra was 80 eV. A sputter etching was made with Argon ions for 1 minute to extract the possible contaminants in the transfer to the samples of the reactor at XPS equipment. Energy calibration was carried by the first component of C1s line aligned to 284.8 eV which corresponds to the binding energy of amorphous carbon [24]. The Shirley background was subtracted during the XPS data fitting. Diffraction patterns (θ-2θ) and rocking curves (ω-2ω) were obtained using Bruker D8 Advance diffractometer equipped with a Cu tube, which provided radiation with a wavelength of 1.54056 Å, and a graphite monochromator in the diffracted beam with an angle of 26.37°. The diffractometer was also equipped with a parallel beam geometry attachment and grazing incidence diffraction was performed with 1° incidence angle. The samples were scanned over the diffraction angle (2θ) range 30°–80° in the step mode with a step size of 0.02°, scan speed of 3s per step and parallel beam voltage of 40 kV and 30 mA current. The Scherrer Equation was used to obtain the stress and crystallite sizes of the samples [25, 26]:

$$\beta_t^2 = \left[ \frac{0.9\lambda}{D\cos\theta} \right]^2 + [4\varepsilon\tan\theta]^2 + \beta_0^2$$  \hspace{1cm} (1)

Where $\beta_t$ is the total broadening of the diffraction line, $\varepsilon$ is the microstrain, $\beta_0$ the instrumental broadening (calculated from quartz calibration standard using Topas R software and the Rietveld method, giving a value approximately 0.03514°), D is the crystallite size, $\lambda$ is wavelength of the ion gun (0.1540 nm), $\theta$ is the Bragg diffracted angle.
The rocking curve were obtained at $2\theta = 38.18^\circ$ ((111) peak direction and around of $\omega = 0.45^\circ$). The data obtained is shown in Table 2. The Park Scientific Instrument model Auto-Probe CP in the mode of AFM-imaging was used to obtain the film thicknesses through the depth profiles.

3. **Results and analysis**

Diffraction patterns ($\theta$-2$\theta$) and rocking curves ($\omega$-2$\omega$) were obtained for the M3, M4, M6, M10, M11, M14 samples and the target (T) (see Figure 1). In this figure the polycrystalline nature of all the samples is clearly demonstrated since all the expected peaks for the Au-$fcc$ structure are observed (with parameters presented in Table 2). We also observe diffraction peaks from stainless steel (SS) because the gold nitride thin films obtained by arc pulsed system are very thin [17, 18]. The lattice parameter obtained from the samples is close to 4.078 Å (the same as the pure gold) oscillating about ±0.003 Å. This value is too small for this XRD measurements, so synchrotron measurements will be required for any further discussion. Changes of texture coefficient of (111) to (200) directions were observed from M3 and M4 samples with respect the other samples (see Table 3 and figures 1 and 2) which have not been observed in any previous reports on gold nitride. Figure 3 shows an overlap of peaks corresponding to directions (111), (200), (311) and (222). Displacements, asymmetries and widening with respect to the target pattern can be observed which may be due to i) the shifts to the higher or lower Bragg angles very common in thin films obtained by Plasma-Assisted Systems (the diffraction peaks are moved to higher angles due to a compressive stress while if diffraction peaks shift to smaller angles it is considered to be due to tensile stress [27]) ii) is also possible to have a new phase through the inclusion of nitrogen atoms in interstitial sites, causing the cubic
lattice planes of gold to be unbalanced, leading to a low crystallinity of the thin film and resulting/deriving in a mechanical flexion of the crystal [18]. This could be verified by small variations or widening of the rocking curves peak (as the unbalanced density in the sample is higher, the rocking curve peak is wider [28]). Figure 4 shows the rocking curves of the gold target (99.999 % Au), M6, M10, M11 and M14 samples. The gold target has a full width at half maximum (FWHM) of 3.671° and a high peak symmetry which confirms the high crystallinity of the target (Table 4). The rocking curves of other samples in this figure 4 exhibit the extra widening of the peaks between 180 to 200% (see table 4) when compared to the rocking curve width obtained for the pure gold target. These widenings could indicate decrease in crystallinity due to dislocation in the crystal as a result of the presence of nitrogen atoms in Au-fcc structure or just changes in a comprehensive/tensile stress properties of samples grown by this method as has been previously reported [18, 28].

In Figure 5a, the rocking curve for M3 and M4 samples are presented which show a low crystallinity due to the low symmetry found. Furthermore, the presence of a shoulder on the left side of the curve suggests the presence of a new peak which could be attributed to the formation of gold nitride species as is corroborated later by XPS analysis (see below). In our previous paper we showed only small changes in the widening of the rocking curves in respect to the direction (111) of the Au-fcc structure [17, 18]. This is very different to the findings that are presented here.

Figure 6a shows the X-ray photoemission spectra of the N1s core levels (narrow energy spectrums) for M3, M4, M6, M10, M11 and M14 samples. It is clear that the samples M3 and M4 exhibit more nitrogen than the rest. The curve fitting of the N1s core level for the samples M10 and M11 was not possible because the nitrogen peak had a very
low intensity (indicative of a low concentration of nitrogen). Lack of nitrogen in these samples could be due to the shortening of the mean free path of the nitrogen ions in the plasma discharge which reduces the probability of nitrogen staying in ionized state, which therefore decreases the reactivity of nitrogen towards gold and consequently the formation of gold nitride species in these samples. Figures 6b and 6c shows the X-ray photoemission spectra of the N1s core levels for, M6, M14, M3 and M4 samples. Samples M6 and M14 exhibit peaks at binding energies of N1s core level spectra at 400.4 eV and 400.5 eV which are a characteristics of N2, oxynitrides or carbonitrdes encapsulated in thin films, the presence of Oxygen and Carbon could be possible to the exposing of the samples at environment, when were transferred of the reactor to XPS equipment, although a sputtering eching for 1 minute was made [3]. A peak at binding energy of 398.1 eV ± 0.3 eV in the M3 sample is a characteristics of gold nitride species [2, 3, 14]. Furthermore, this energy is in a range between 396.0 to 398.0 eV ± 0.2 eV, which are typically attributed to nitrogen hybridization with transition metals [13, 17, 29]. The M4 sample shows a peak at binding energy 398.3 ± 0.3 eV, this energy is close to 398.0 eV within the error; which can also be attributed to gold nitride species [14].

Table 2. Data obtained from XRD. 3rd and 5th columns are the comparison with data obtained from the pure gold target.

<table>
<thead>
<tr>
<th>Samples</th>
<th>FWHM (grades)</th>
<th>FWHM increase in respect to Gold Target (percentage)</th>
<th>Position (2θ)</th>
<th>In respect to Gold Target (displacements)</th>
<th>Lattice Parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold Target</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 1 1</td>
<td>0.046</td>
<td>1</td>
<td>38.18</td>
<td>0</td>
<td>4.078 ± 0.007</td>
</tr>
<tr>
<td>2 0 0</td>
<td>0.103</td>
<td>1</td>
<td>44.39</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3 1 1</td>
<td>0.186</td>
<td>1</td>
<td>64.58</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2 2 2</td>
<td>0.241</td>
<td>1</td>
<td>77.56</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>M3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 1 1</td>
<td>0.533</td>
<td>11.58</td>
<td>38.21</td>
<td>0.03</td>
<td>4.078 ± 0.024</td>
</tr>
<tr>
<td>2 0 0</td>
<td>0.388</td>
<td>3.76</td>
<td>44.48</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>3 1 1</td>
<td>0.758</td>
<td>4.07</td>
<td>64.68</td>
<td>0.10</td>
<td></td>
</tr>
</tbody>
</table>
It is clearly observed that, the presence of different species in the samples noticeably influences the Bragg diffraction lines (both diffraction patterns and rocking curves). The coefficient of the crystallographic texture was calculated between the directions (111) and (200) by the following equations [27]:

\[ Tc = \frac{I(111)}{I(111)+I(200)} \quad \text{and} \quad Tc = \frac{I(200)}{I(111)+I(200)} \]  

(1)

where Tc is the texture coefficient and I is the intensity of the peaks observed in the diffraction pattern. The samples M6, M14 (which have N₂ species unhybridized with gold) and M10, M11 (which have only gold species) show a preferential crystallographic orientation (111) which is characteristic of the Au-fcc structure. However the M3 and M4 samples presents a dispute between the preferential orientations (111) and (200) having a slight crystallographic orientation (200) advantage (see Table 4 and figure 2). We attribute this observed change in crystallographic orientation to the presence of gold nitride species.
in the M3 and M4 samples. In figure 2 the micro-stress and crystallite size of the samples are shown. The micro-stress increases with the appearing of gold nitride species in the samples, besides that, the samples with on average higher crystallite size are M10 and M11. From XPS is clear that M10 and M11 possess a single species of atoms (Au species), which possibly helps to have much larger grains of the sample, which than lead to one preferential crystallographic orientation (111). This implies then, that the homogenization of the thin films with a single crystallite size, strongly depends on the present species in the sample. Gold nitride species, Au or N\textsubscript{2} may block the formation of a regular crystallite size, leading to a dispute distribution of different crystallite sizes during coalescence of islands, preventing the growth of a strong free crystallite size, as seen in the M10 and M11 samples (where only species of Au are present) [30].

**Table 3.** Texture coefficient, crystallite size, microstrain and thickness present in the samples.

<table>
<thead>
<tr>
<th>SAMPLES</th>
<th>TEXTURE COEFFICIENT (dimensionless)</th>
<th>CRYSSTALLITE SIZE (nm)</th>
<th>MICROSTRAIN (dimensionless)</th>
<th>THICKNESS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(111)</td>
<td>(200)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M3</td>
<td>0.43</td>
<td>0.57</td>
<td>30 ± 23</td>
<td>400 ± 129</td>
</tr>
<tr>
<td>M4</td>
<td>0.48</td>
<td>0.52</td>
<td>23 ± 25</td>
<td>415 ± 143</td>
</tr>
<tr>
<td>M6</td>
<td>0.72</td>
<td>0.28</td>
<td>15 ± 3</td>
<td>442 ± 96</td>
</tr>
<tr>
<td>M10</td>
<td>0.66</td>
<td>0.44</td>
<td>45 ± 10</td>
<td>428 ± 129</td>
</tr>
<tr>
<td>M11</td>
<td>0.70</td>
<td>0.30</td>
<td>43 ± 35</td>
<td>418 ± 162</td>
</tr>
<tr>
<td>M14</td>
<td>0.76</td>
<td>0.24</td>
<td>29 ± 3</td>
<td>408 ± 100</td>
</tr>
</tbody>
</table>

The widening observed for the rocking curves of M3 and M4 samples (see table 4) could be attributed to the presence of different species (Au, N\textsubscript{2} or AuN) as determined by the XPS of the N1s core levels. An overlay of the rocking curves for the samples M10 and M11 (which are contain only Au species) is presented in Figure 5b. A strong widening in respect to the rocking curve of the pure gold target and also shifts (to the right or left) of the
diffraction lines is observed which is due to the tensile/residual micro-stress that are present in the grown samples [27]. Figure 5c shows an overlay of rocking curves for samples M6 and M14 (these samples contain species such as N₂, oxynitrides or carbonitrides). Rocking curves for samples M6 and M14 show the same widening but their shape is not affected (as previously observed for samples M3 and M4, see figure 5a). This also implies that the strong deformation and change of orientation of crystallographic planes is related to the presence of gold nitride species.

Table 4. Broadening of the rocking curves of samples respect to the pure gold.

<table>
<thead>
<tr>
<th>Sample</th>
<th>FWHM</th>
<th>Percentage increase Vs Gold Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>3.671°</td>
<td>N/A</td>
</tr>
<tr>
<td>M3</td>
<td>9.199°</td>
<td>250.58 %</td>
</tr>
<tr>
<td>M4</td>
<td>9.600°</td>
<td>261.51 %</td>
</tr>
<tr>
<td>M6</td>
<td>6.675°</td>
<td>181.83 %</td>
</tr>
<tr>
<td>M10</td>
<td>6.801°</td>
<td>185.62 %</td>
</tr>
<tr>
<td>M11</td>
<td>6.508°</td>
<td>177.28 %</td>
</tr>
<tr>
<td>M14</td>
<td>7.593°</td>
<td>206.83%</td>
</tr>
</tbody>
</table>

3.1 Modelling the AuN and Au+N₂ influential curves

We have mainly considered two equivalent classes of the experiments and we wish to differentiate between a diatomic molecule AuN and two isolated components, Au and N₂, in these experiment.

Our main aim is to provide a model that explains cases represented in figure 5a to figure 5c, or vice versa, in such way that for a given experiment the model can identify automatically the corresponding family. An extra effort must be made to obtain the relationship among the coefficients of the model and the experimental parameters. Our preference experiment must be very close to figure 5a and avoid figure 5c.
Firstly we need to transform curves of figure 5a and 5c into special smooth functions which will preserve all the geometrical information of the curves. We will essentially use the well-studied theory of non-parametric regression with contaminated homoscedastic predictors [31].

Fixing the original curves of figures 5a and 5c we obtain certain smooth functions (say, \( u = g_1(v) \) and \( u = g_2(v) \), see figures 7a and 7b respectively) that define its geometry and main properties. It is clear that these functions are not linear, so we model them by some fitting curves procedure or instead of transforming them in order to obtain linearity we can model the relationship between the outlier and the leverage characteristics of the points in each curve under the linear model.

We recall that in a linear model \( Y = X\beta + \varepsilon \). The least squares estimation of \( \beta \) is given by

\[
\hat{\beta} = (X'X)^{-1}X'Y
\]

and

\[
A = (a_{ii}) = X(X'X)^{-1}X' \text{ is the orthogonal projection of } Y \text{ onto the space spanned by } X \text{ i.e. } \hat{Y} = AY,
\]

where the elements of \( A \) are called leverages and are useful for diagnostics of the errors in the linear model [32, 33]. Leverages give a measure of how far a case is from a typical value. Thus, the i-th diagonal element \( a_{ii} \) of the matrix represents the potential effect that the i-th observed target value \( Y_i \) can have on the i-th fitted value \( \hat{Y}_i \). The leverage of any point in the above deconvolved function will constitute the ordinate of the next function and the corresponding abscissa is obtained by considering the so called jackknife residuals of the referred point [32] which explains the outlier characteristic of the point; i.e. how the point fits the linear model. This property is modeled by the jackknife residual \( t_i = \frac{\hat{\varepsilon}_i \sqrt{1 - h_i}}{\hat{\sigma}_{(i)}} \), where \((i)\) denotes that the i-th case that has been excluded and \(\hat{\varepsilon}\) and \(\hat{\sigma}\) represent the estimation of the errors and their standard deviation.
Combination of the jackknife and leverage characteristics give rise to the influential potential of the corresponding point, which is a final refined function that provides the model for separating the classes of AuN, Au and N\textsubscript{2}. So, if we obtain the jackknife and leverage of each point \((v, u)\) in deconvolved functions \(u = g_1(v)\) and \(u = g_2(v)\) of figures 7a and 7b, we obtain the so called influential curves \([31, 32]\) \(r = l_1(s)\) and \(r = l_1(s)\).

Both classes of curves (present in the figures 10 and 11) are clearly differentiated and they are just right to be model by obtaining a parametric curve which fits them accurately. It is easy to see that the required model which has such a similar influential curve is a cubic polynomial of the form:

\[
\mathbf{u}(\mathbf{v}) = \mathbf{v}^3 + q\mathbf{v}^2 + l\mathbf{v}.
\]

This deconvolved model depends on the quadratic and linear coefficients \(q\) and \(l\). An independent term is not necessary because the vertical translation invariance of the influential curve, the cubic coefficient is a fixed one in order to obtain naturally the degenerated quadratic model.

In order to model the AuN and Au+N\textsubscript{2} influential curves of figures 8a and 8b, we construct an algorithm which sweeps the coefficients \(q\) and \(l\) in wide domain and obtain the minimum Riemaniann distance (RD) \([31, 32]\). Taking into account the continuity of the influential curves and the simplicity of the cubic model we can propose any initial value emphasizing the \(q\) parameter which retains the main shape of the curves. The procedure is also improved by considering (a thousand times of resample) of the two figures with 200 points selected randomly. Then a basic summary of the distances are constructed and a consistent estimation of the minimum RD is median that gives the corresponding \(q\) and \(l\).
In the case of the AuN influential curve (figure 8a), the last iterations for the estimation of the coefficients q and l and the summary of the RD to the cubic influential curve are given in table 5.

So a suggested influential cubic curve for the experimental AuN curve is considered as:

\[ u(v) = v^3 - 2.23v^2 + 0.80v \]

with a notable Riemann distance near to the median 0.057.

For the Au+N\textsubscript{2} influential curve shown in figure 8b, the stability of the last iterations involving figures of 200 points, 1000 times resampled, is summarized in table 6.

Table 5. Estimations of the coefficients q and l to AuN influential curve

<table>
<thead>
<tr>
<th>q</th>
<th>l</th>
<th>Min.</th>
<th>1st Qu.</th>
<th>Median</th>
<th>Mean</th>
<th>3rd Qu.</th>
<th>Max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.13</td>
<td>0.98</td>
<td>0.114</td>
<td>0.125</td>
<td>0.127</td>
<td>0.126</td>
<td>0.129</td>
<td>0.130</td>
</tr>
<tr>
<td>-1.27</td>
<td>0.90</td>
<td>0.108</td>
<td>0.112</td>
<td>0.116</td>
<td>0.116</td>
<td>0.118</td>
<td>0.123</td>
</tr>
<tr>
<td>-1.42</td>
<td>0.83</td>
<td>0.090</td>
<td>0.094</td>
<td>0.098</td>
<td>0.098</td>
<td>0.104</td>
<td>0.105</td>
</tr>
<tr>
<td>-1.60</td>
<td>0.77</td>
<td>0.071</td>
<td>0.080</td>
<td>0.085</td>
<td>0.084</td>
<td>0.088</td>
<td>0.091</td>
</tr>
<tr>
<td>-1.80</td>
<td>0.71</td>
<td>0.065</td>
<td>0.069</td>
<td>0.071</td>
<td>0.072</td>
<td>0.075</td>
<td>0.080</td>
</tr>
<tr>
<td>-2.03</td>
<td>0.70</td>
<td>0.056</td>
<td>0.061</td>
<td>0.062</td>
<td>0.062</td>
<td>0.063</td>
<td>0.065</td>
</tr>
<tr>
<td>-2.18</td>
<td>0.75</td>
<td>0.054</td>
<td>0.058</td>
<td>0.058</td>
<td>0.058</td>
<td>0.059</td>
<td>0.062</td>
</tr>
<tr>
<td>-2.23</td>
<td>0.80</td>
<td>0.055</td>
<td>0.057</td>
<td>0.058</td>
<td>0.058</td>
<td>0.059</td>
<td>0.062</td>
</tr>
<tr>
<td>-2.23</td>
<td>0.80</td>
<td>0.053</td>
<td>0.056</td>
<td>0.057</td>
<td>0.057</td>
<td>0.058</td>
<td>0.061</td>
</tr>
</tbody>
</table>

This curve is more problematic because it is less symmetric than the preceding one, but the method converges near to median of 0.104 and a suggested influential cubic curve for the experimental Au+N\textsubscript{2} curve is considered as:

\[ u(v) = v^3 + 20.36v^2 - 0.84v \]

The last iterations for the estimation of the coefficients q and l and the summary of the RD to the cubic influential curve are given in table 6.
Table 6. Estimation of the coefficients q and l to Au+N$_2$ influential curve.

<table>
<thead>
<tr>
<th>q</th>
<th>l</th>
<th>Min.</th>
<th>1st Qu.</th>
<th>Median</th>
<th>Mean</th>
<th>3rd Qu.</th>
<th>Max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.04</td>
<td>-1.16</td>
<td>0.100</td>
<td>0.101</td>
<td>0.102</td>
<td>0.104</td>
<td>0.108</td>
<td>0.110</td>
</tr>
<tr>
<td>19.51</td>
<td>-1.30</td>
<td>0.102</td>
<td>0.105</td>
<td>0.106</td>
<td>0.106</td>
<td>0.107</td>
<td>0.110</td>
</tr>
<tr>
<td>20.97</td>
<td>-1.14</td>
<td>0.089</td>
<td>0.107</td>
<td>0.109</td>
<td>0.108</td>
<td>0.112</td>
<td>0.113</td>
</tr>
<tr>
<td>19.40</td>
<td>-1.11</td>
<td>0.098</td>
<td>0.103</td>
<td>0.104</td>
<td>0.106</td>
<td>0.119</td>
<td>0.114</td>
</tr>
<tr>
<td>19.89</td>
<td>-1.08</td>
<td>0.093</td>
<td>0.107</td>
<td>0.108</td>
<td>0.107</td>
<td>0.119</td>
<td>0.115</td>
</tr>
<tr>
<td>19.39</td>
<td>-1.00</td>
<td>0.099</td>
<td>0.104</td>
<td>0.110</td>
<td>0.108</td>
<td>0.112</td>
<td>0.115</td>
</tr>
<tr>
<td>19.87</td>
<td>-0.88</td>
<td>0.098</td>
<td>0.100</td>
<td>0.106</td>
<td>0.105</td>
<td>0.109</td>
<td>0.114</td>
</tr>
<tr>
<td>19.38</td>
<td>-0.77</td>
<td>0.092</td>
<td>0.106</td>
<td>0.109</td>
<td>0.107</td>
<td>0.112</td>
<td>0.113</td>
</tr>
<tr>
<td>19.86</td>
<td>-0.75</td>
<td>0.102</td>
<td>0.105</td>
<td>0.107</td>
<td>0.107</td>
<td>0.109</td>
<td>0.110</td>
</tr>
<tr>
<td>20.36</td>
<td>-0.84</td>
<td>0.103</td>
<td>0.103</td>
<td>0.104</td>
<td>0.106</td>
<td>0.105</td>
<td>0.113</td>
</tr>
</tbody>
</table>

It is important to note the strong difference between the two influential cubic curves, in particular the leading coefficients q are different not only in magnitude but in sign. Note that the complexity of the Au+N$_2$ is reflected by the fact that it is more unstable which can be explained by the collapsing and non-symmetric curve which is opposite to the stability of the AuN noticed in the equilibrium and symmetry of such curve. This coefficient q could be an indicator of structural changes between Au $fcc$ to AuN that will be studied further in future work.

Previous theoretical works have predicted that the most stable gold nitride phase is Au$_3$N as a triclinic metallic phase [3, 19]. However recently it was noted that experimentally determined better hardness of gold nitride when compared to pure gold [11] is likely to be due to properties of gold nitride at lower dimensions [19] and the negative cohesive energy of the most stable AuN phase, B17, was determined [19].

4. Conclusions

The gold nitride species were obtained within an Au thin film using an arc pulsed system - PAPVD on 304 stainless steel. The change in the orientation of crystallographic
planes of (111) to (200) in the gold diffraction pattern and a strong deformation of rocking curves are due the increase of the amount of gold nitride species in the Au thin films. A part of the asymmetries, widening and shifts of the diffraction Bragg lines were attributed to the presence of gold nitride species which have also been detected also by XPS of the N1s core levels at the binding energies of 398.1 eV and 398.3 eV.

This work proposes a method to separate experimental curves of AuN with Au in different proportions and their relation with curves of grown Au and crystallographic Au. Transformations of rocking curves by shape theory, deconvolution and influential curves has led to a simple cubic polynomial fitting of curves which enables the determination of their coefficients in such a way that suggests the cubic crystallinity behavior of the gold nitride structures.

5. ACKNOWLEDGMENTS

We thank the Vice-rectoría de Investigaciones de la Universidad de Medellín (grant number 745) and Instituto Colombiano para el Desarrollo de la Ciencia y la Tecnología (COLCIENCIAS) within the programe “doctorados nacionales en la II Convocatoria Nacional de Apoyo a Programas de Posgrado 2006” for financial support of this work. We also thank M. Pugh for critical reading of the manuscript.

REFERENCES


Figure captions

**Figure 1.** X-ray diffraction patterns of T (pure gold target), M3, M4, M6, M10, M11 and M14 samples prepared by arc pulsed-PAPVD varying the nitrogen pressure at discharge moment (for parameters of synthesis see table 1).

**Figure 2.** a) Lattice Parameter, b) Texture coefficient, c) Microstrain and d) Crystallite Size for samples prepared by pulsed-PAPVD (for parameters of synthesis see table 1).

**Figure 3.** Superposition of (111) (a and b), (200) (c and d), (311) (e and f) and (222) (g and h) peaks to Au-fcc structure. At the left are figures about widening and at the right are figures about shifts to high or low Bragg angles; both are with respect to the pure gold target (T).

**Figure 4.** Superposition of rocking curves for all samples (M3, M4, M6, M10, M11 and M14) and pure gold target (T).

**Figure 5.** Rocking Curves Superposition a) M3 and M4 samples, b) M10 and M11 samples and c) M6 and M14 samples.

**Figure 6.** a) N1s narrow spectrums for M3, M4, M6, M10, M11 and M14 samples. It can observe the change of the N1s spectral line due to the amount of nitrogen, Binding energies b) M6 and M14 samples and c) M3, M4 samples.

**Figure 7.** Deconvolved transformation function a) figure 5a and b) figure 5c.

**Figure 8.** Influential curve a) for AuN and b) for Au+N$_2$. 
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Figure 8
HIGHLIGHTS

- We obtained change in the orientation of crystallographic planes of (111) to (200) in the gold diffraction pattern due the increase of the amount of gold nitride species in the Au thin films.
- A part of the asymmetries, widening and shifts of the diffraction Bragg lines were attributed to the presence of gold nitride species.
- A method to separate experimental curves of AuN with Au in different proportions was obtained.