Surface & Coatings Technology 309 (2017) 249–257

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Rocking curves of gold nitride species prepared by arc pulsed - physical assisted plasma vapor deposition

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A R T I C L E I N F O

Article history:
Received 19 September 2016
Revised 21 November 2016
Accepted in revised form 22 November 2016
Available online 24 November 2016

Keywords:
Gold nitride
Rocking curve
Influential curves
Asymmetries

A B S T R A C T

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.

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 96.7 ± 0.2 eV) [2,3], laser ablation (no reported) [6,7], arc pulsed (with a binding energy of 398.1 ± 0.2 eV) [13] and reactive ion sputtering (with a binding energy of 397.7 ± 0.2 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) modelling of the rocking

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

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

Samples	M3	M4	M6	M10	M11	M14
Pressure (mbar)	3.5	4.0	5.0	7.0	7.5	8.0
Arcs number	3					
Gas	Nitrogen					
Voltage (volts)	200					
Temperature (°C)	140					

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 1×10^{-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.

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 min 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

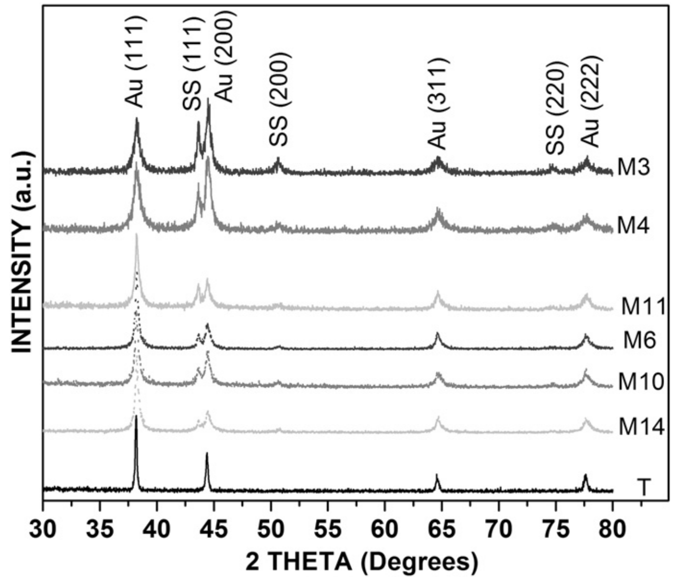

Fig. 1. X-ray diffraction patterns of T (pure gold target), M3, M4, M6, M10, M11 and M14 samples prepared by arc pulsed-PAPVD varying the nitrogen pressure at discharge moment (for parameters of synthesis see Table 1).

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

Samples		FWHM (grades)	FWHM increase in respect to gold target (percentage)	Position (2θ)	In respect to gold target (displacements)	Lattice parameter (Å)
Gold target	1 1 1	0.046	1	38.18	0	4078 ± 0,007
	2 0 0	0.103	1	44.39	0	
	3 1 1	0.186	1	64.58	0	
	2 2 2	0.241	1	77.56	0	
M3	1 1 1	0.533	11.58	38.21	0.03	4078 ± 0,024
	2 0 0	0.388	3.76	44.48	0.09	
	3 1 1	0.758	4.07	64.68	0.10	
	2 2 2	0.875	3.62	77.62	0.06	
M4	1 1 1	0.643	13.97	38.18	0	4075 ± 0,018
	2 0 0	0.461	4.48	44.51	0.12	
	3 1 1	0.452	2.43	64.58	0	
	2 2 2	1.054	4.37	77.59	0.03	
M6	1 1 1	0.572	12.43	38.24	0.06	4076 ± 0,015
	2 0 0	0.723	7.01	44.57	0.18	
	3 1 1	0.463	2.49	64.62	0.04	
	2 2 2	0.915	3.79	77.74	0.18	
M10	1 1 1	0.349	7.58	38.21	0.03	4078 ± 0,017
	2 0 0	0.389	3.77	44.42	0.03	
	3 1 1	0.599	3.22	64.93	0.35	
	2 2 2	0.703	2.91	77.58	0.02	
M11	111	0.391	8.50	38.21	0.03	4076 ± 0,013
	200	0.311	3.01	44.38	−0.01	
	311	0.463	2.48	64.59	0.01	
	222	0.696	2.89	77.61	0.04	
M14	111	0.364	7.91	38.25	0.06	4076 ± 0,018
	200	0.429	4.16	44.49	0.10	
	311	0.537	2.89	64.73	0.14	
	222	0.655	2.72	77.62	0.06	