Applied Surface Science 302 (2014) 124–128

Contents lists available at ScienceDirect

Applied Surface Science

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

The effect of deposition atmosphere on the chemical composition of TiN and ZrN thin films grown by pulsed laser deposition

D. Craciun [a], G. Socol [a], N. Stefan [a], G. Dorcioman [a], M. Hanna [b], C.R. Taylor [b], E. Lambers [c], V. Craciun [a,*]

[a] Laser Department, National Institute for Laser, Plasma, and Radiation Physics, Bucharest—Magurele, Romania
[b] Mechanical and Aerospace Engineering, University of Florida, Gainesville, FL 32611, USA
[c] Major Analytical Instrumentation Center, College of Engineering, University of Florida, Gainesville, FL 32611, USA

ARTICLE INFO

Article history:
Received 30 June 2013
Received in revised form 14 October 2013
Accepted 14 October 2013
Available online 23 October 2013

Keywords:
TiN, ZrN
Hard coating
Pulsed laser deposition
X-Ray diffraction

ABSTRACT

Very thin TiN and ZrN films (<500 nm) were grown on (1 0 0) Si substrates at temperatures up to 500 °C by the pulsed laser deposition (PLD) technique using a KrF excimer laser under residual vacuum or various mixtures of CH_4 or N_2. Auger electron spectroscopy investigations found that films contained a relatively low oxygen concentration, usually below 3.0 at%. Films deposited under residual vacuum or very low N_2 pressures (<3×10^{-3} Pa) contained 3–6 at% C atoms in the bulk. This fraction grew to 8–10 at% when the deposition was performed under an atmosphere of 2×10^{-3} Pa CH_4. To avoid C atoms incorporation into the bulk a deposition pressure of 10 Pa N_2 was required. X-ray photoelectron spectroscopy investigations found that oxygen was mostly bonded in an oxynitride type of compound, while carbon was bonded into a metallic carbide. The presence of C atoms in the chemical composition of the TiN or ZrN improved the measured hardness of the films.

1. Introduction

Transition metal nitrides TiN and ZrN possess both ceramic and metallic characteristics, which explain their excellent properties: very high melting points [1], high hardness (30–35 GPa) [2–5], good wear resistance [6,7], high thermochemical stability [8,9], low electrical resistivity [10], low work function [11], and good biocompatibility [12].

For applications in microelectronics, MEMS or nuclear technology, there is a need for rather thin and high quality films. Pulsed laser deposition (PLD) technique was shown to be able to grow such thin films at moderate substrate temperatures, below 550 °C [13–15]. The role of the deposition atmosphere on the chemical composition and properties of thin films deposited by PLD has been investigated in great detail [16–18]. When the deposition atmosphere plays a major role in the final chemical composition of the deposited film, which could be different from that of the ablated target, as in the case of TiN deposition from metallic Ti target under N_2 atmosphere, the technique was called reactive PLD [19,20]. Ti and Zr atoms are very reactive and easily interact with the gaseous atmosphere. Therefore, it is expected that the deposited films could contain oxygen and carbon atoms collected from the residual vacuum besides those intentionally introduced during deposition. The chemical composition of TiN and ZrN films deposited under residual vacuum or various mixtures of CH_4 and N_2 and its effect on the films structure and properties has been investigated and the results are presented below.

2. Experimental details

The PLD experimental set up used to deposit the films has been extensively described previously [13–15] and is only schematically described here. It uses a KrF excimer laser ($\lambda = 248$ nm, pulse duration $\tau = 25$ ns, 6 to 8 J/cm^2 fluence, 40 Hz repetition rate) to ablate TiN or ZrN polycrystalline targets (Plasmaterials, Inc.) in a stainless steel chamber. The ultimate pressure in the deposition chamber was in the low 10^{-6} Pa range to avoid as much as possible incorporation of oxygen atoms from the residual gases. The films were deposited on p^{2+} (1 0 0)Si substrates (MEMC Electronic Materials, Inc.) at nominal substrate temperatures of 300 and 500 °C under residual vacuum or a high purity atmosphere of CH_4 or N_2. The deposition conditions are displayed in Table 1.

A Panalytical X'Pert MRD instrument working with Cu $K\alpha$ radiation and set up in a parallel beam geometry was used to acquire X-ray reflectivity (XRR) curves and X-ray diffraction patterns (both grazing and symmetrical incidence, GIXD and XRD) from the deposited films. The films mass density, thickness, and surface roughness were obtained from simulations of the XRR curves using

* Corresponding author. Tel.: +40 212303378.
E-mail address: valentin.craciun@inflpr.ro (V. Craciun).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.10.095

Table 1
Deposition conditions, lattice parameter, density, surface roughness, structural and mechanical properties of the deposited films.

Sample	Atmosphere [Pa]	Number of pulses	Lattice parameter [Å]	Density [g/cm^3]	Roughness [Å]	Grain size [Å]	Strain [%]	E [GPa]	H [GPa]
ZrN1	2×10^{-3} CH_4	20,000	4.684			110	0.9	245	32.5
ZrN2	2×10^{-2} CH_4	20,000	4.668	7.15	7	111	1.4	270	35.2
ZrN3	2×10^{-3} N_4	20,000	4.667			155	1.3	255	34.5
ZrN4	2×10^{-2} N_2	20,000	4.681	7.13	9	79	0.7	252	34.3
ZrN5	Vacuum	20,000	4.629	7.15	10	40	0.2	201	23.3
TiN_28	Vacuum	30,000	4.242	5.40	8	168	0.9	363	40.2
TiN_29	10 N_2	30,000	4.252	5.23	10	214	0.7	391	35.1
TiN_2 C	1×10^{-1} N_2	30,000	4.243	5.24	9	227	1.0	363	38.7

Table 2
Structural and mechanical properties of the deposited ZrN and TiN films.

Sample	Grain size (Å)	Micro-strain (%)	E (GPa)	H (GPa)
ZrN1	110	0.9	245	32.5
ZrN2	111	1.4	270	35.2
ZrN3	155	1.3	255	34.5
ZrN4	79	0.7	252	34.3
ZrN5	41	0.2	201	23.3
TiN_28	168	0.9	363	40.2
TiN_29	214	0.7	391	35.1
TiN_2C	227	1.0	363	38.7

a model consisting of three layers: interfacial layer, accounting for the silicon native oxide and any ions that were subplanted/mixed within this layer [21,22], the deposited nitride layer and a surface contamination layer accounting for the hydroxide/carbon layer present at the topmost surface when films were exposed to the ambient Table 2.

The residual stress of the deposited films was obtained by acquiring GIXD patterns at various tilting angles ψ, or acquiring offset scans and plotting the d-space values versus $\cos^2\alpha\sin^2\psi$ technique, where $\alpha=\theta-\omega$ [23]. The crystallite size and microstrain were evaluated from Williamson and Hall plots [24] with the diffraction line parameters being extracted from the GIXD patterns. Atomic force microscopy (AFM) and field-emission scanning electron microscopy (FE-SEM) images of surface and cross sections of fractured films as well as nanoindentation sites were also recorded.

The chemical composition of the deposited films was investigated by Auger electron spectroscopy (AES) in a Perkin-Elmer PHI 660 system (5 kV, 30° take off angle) and by X-ray photoelectron spectroscopy (XPS) in a Perkin-Elmer PHI 5100 ESCA system using Mg $K\alpha$ radiation. AES and XPS survey or high resolution spectra were collected after various time cycles of Ar ion sputtering (4 kV, 1–3 μA/cm^2; for XPS measurements the Ar ion beam was rastered over an area of 10×7 mm^2). The mechanical properties of the thin films were investigated using a nanoindentation device (Triboindenter, Hysitron, Inc.) equipped with a cube-corner diamond tip. The indentation experiments were performed in load control, with maximum loads ranging from 750 to 5 μN. To minimize substrate contributions, the hardness and reduced modulus were determined from load–displacement contact depths between 20 and 30 nm, as described previously [15] following the model of Oliver and Pharr [26].

3. Results and discussion

XRR curves acquired from TiN and ZrN films deposited under residual vacuum or low pressure of N_2 and CH_4 are displayed in Fig. 1. One could observe that the value of the critical angle of the ZrN film deposited under residual vacuum is slightly smaller than that of the sample deposited under 2×10^{-2} Pa N_2, indicating a lower mass density. From simulations of the acquired XRR curves we obtained values for the films density and surface roughness that are also shown in Table 1. The thickness of the top contamination layer was around 2.5 to 3.5 nm and its density from around 3 to 4 g/cm^3, indicative of an oxyhydride layer.

GIXD patterns acquired from the deposited films are displayed in Fig. 2. All present peaks correspond to the rock-salt lattice of TiN and ZrN [25]. It is obvious that the TiN diffraction peaks were narrower than those of ZrN films, indicative of larger crystallite sizes. Symmetrical XRD scans showed that films were slightly (1 1 1) textured, a typical texture for rock-salt type structures, where (1 1 1) planes have the highest atomic density. Williamson-Hall plots ($B\times\cos\theta_B$ versus $\sin\theta_B$, where B is the full width at half maximum of the GIXD peaks, which was corrected for instrumental broadening, and θ_B is the Bragg angle), were used to estimate the crystallite sizes and micro-strain values which are also displayed in Table 1. The crystallite size and lattice parameter of the ZrN films deposited under vacuum had the smallest values, increasing when a CH_4 atmosphere was used during deposition. There was no obvious trend for the TiN films analyzed here. The rather large values estimated for the micro-strain were caused by defects induced by energetic ions and atoms from the plasma that bombarded the growing film during deposition [21,22].

From the slope of relative lattice parameter changes, $(a-a_0)/a_0$ versus $\cos^2\alpha\times\sin^2\psi$, where a_0 is the lattice parameter calculated from the 2 theta position of the (1 1 1) peak acquired using the symmetrical geometry, ψ is the tilting angle and α the offset angle ($\alpha=\theta_{\equiv}-\omega$, ω being the grazing incidence angle) compressive strain values of the order of −4 to −6 GPa were estimated for these thin films, typical for the strong ions and atoms bombardment during growth [27]. Measurements of the substrate curvature radius obtained from the measurement at different locations of the ω shift of the (0 0 4)Si substrate diffraction line confirmed the XRD estimated residual stress values.

FE-SEM investigations of the fractured films showed that the films thickness was around 400 nm and 500 nm for ZrN and TiN, respectively, and possessed a very compact structure. At very high magnifications it was easier to observe individual crystallites for the TiN films, since their dimensions were larger, confirming the values estimated from the analysis of the XRD patterns.

AES high resolution survey spectra, as those shown in Fig. 3, recorded from the as-deposited surface and after removal of more than 10 nm of surface material by Arion sputtering, indicated oxygen concentrations below 3 at% within the deposited films. The Zr to N ratios were larger than 1.3, indicating a substoichiometric compound, more so for films deposited under vacuum.

XPS investigations as those displayed in Fig. 4 showed that the binding energy of C atoms, when present in bulk, was around 282.5 eV, corresponding to C bonded in a metallic carbide type of compound. It has been reported that C atoms incorporated within TiN films form a graphite type of compound [28]. However, for PLD films, the high energy of incoming ions and atoms promoted the chemical reaction between the C and Ti atoms. It is interesting to note that the TiN film deposited under 10 Pa N_2 atmosphere did not contain C atoms in bulk.

The complex bonding in these films can clearly be seen from high resolution scans recorded for the Zr 3d peak region shown