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Structural, morphological and mechanical characterization of Mo sputtered coatings

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ABSTRACT

In this work, the intrinsic properties of molybdenum films deposited by DC magnetron sputtering (DCMS) on titanium substrates have been investigated, as a function of working gas (Ar, Kr, Xe) and pressure. Morphology, microstructure, hardness, elastic modulus, and residual stress have been studied through high resolution methodologies. Microstructural analyses consisted of Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and focused ion beam (FIB) cross section analysis. Moreover, nano-mechanical properties of the films (hardness and modulus) were analyzed by nano-indentation testing while adhesion was evaluated by scratch tests. A recently proposed approach was used to investigate the average residual stress of the produced coatings. It involves incremental FIB milling of annular trenches at material surface, combined with high resolution SEM imaging [1]. SEM–FIB and XRD results showed a significant modification of films' microstructure due to selected deposition parameters: it goes from dense-columnar (high crystallite size) at low working pressure and/or high gas mass to nano-porous (small grains) at high pressure and/or low gas mass. This means that the momentum flux carried to the substrate considerably change. In addition residual stress field and mechanical property results are consistent with the coatings' microstructure variations and can be successfully used to confirm them. Finally, it has been found that microstructure and/or mechanical properties of the coatings help to foresee the film/substrate system adhesion. This is fundamental to predict its functional behavior.
Therefore, an effective route to tailor the structure and properties of molybdenum coatings was investigated. Modifying synthesis conditions, Mo films can present dense microstructures and good mechanical properties (high Young's modulus and load bearing capacity) demonstrating their potential for applications in harsh environments like thermonuclear fusion plants. Otherwise changing sputtering parameters, they can show a nano-porous structure, suggesting novel applications as for example in the lubrication and catalysis fields.

1. Introduction

Because of molybdenum's remarkable properties, its coatings have been used in various technological areas such as microelectronics [2], back contacts for solar cells [3], and superconducting microcalorimeters for high performance radiation detectors [4]. Moreover molybdenum films (2–3 μm thick) are used for nuclear energy applications [5] and missile and aircraft parts. As a consequence of their appeal, a variety of deposition techniques and conditions has been employed to obtain Mo coatings.

Most of the works have focused on thin films (<1 μm thick), where researchers analyzed early-stage film nucleation and growth.

Increasing thickness, large residual stress could lead to either, film delamination and buckling under compression [6], or film cracking and de-cohesion under tension [7], causing serious practical problems. In an effort to understand and ultimately control these stresses, a number of studies have been conducted over the past decades [8].

Bias voltage, working gas pressure and atomic mass of the incident ions are well-known parameters to induce modifications in the properties of the sputtered films (such as stress, hardness, grain size, density and crystal structure). Working pressure has perhaps been the most studied variable to date in terms of residual stress, and there is an almost universally observed transition from tension to compression as pressure is decreased [9–14].

Another well-studied variable in the sputtering process is the effect of substrate biasing, where a negative potential applied to the growing film has been shown to induce compressive stress [15–19]. These empirical observations have been broadly rationalized based on the atomic peening mechanism; decreasing sputtering gas pressure and increasing substrate bias both lead to high kinetic energy conditions, tending to

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yield compressively stressed deposits. Striking a balance between tensile and compressive mechanisms, it should be possible to find a low stress condition for a given experimental setup by simple adjustment of the sputtering gas pressure and/or application of substrate biasing. Furthermore, modifying deposition parameters it is possible to affect properties such as hardness (H) and elastic modulus (E). Depending on the changes, properties such as H, resistance to plastic deformation, elastic strain to failure capability, resilience and toughness can be optimized for specific applications.

The present work was focused on low temperature DC magnetron sputtering experiments, paying attention to variables that significantly control the kinetic energy of the deposition process: sputtering gas mass (Ar, Kr, Xe) and working pressure. Mo films have been deposited on titanium coupons maintaining a constant applied bias voltage ($-40\ V_{DC}$).

An innovative single instrument FIB milling and imaging technique has been used to examine the residual stress state in Mo films, namely the micron-scale ring-core method. Sub-micron resolution for stress evaluation has been achieved and allowed to perform stress–structure–property correlations [20]. Residual stress measurements together with morphology and crystal structure analyses, hardness, elastic modulus and adhesion evaluations provide a complete understanding of the prospective performance of the coating. Therefore this systematic approach permits on the one hand the deep knowledge on the molybdenum film properties, on the other hand to control the deposition conditions to direct the coating characteristics.

2. Experimental details

2.1. Film deposition

Several samples were prepared by depositing Mo films (thickness range 1.8–2.9 μm) by DC magnetron sputtering (DCMS) on titanium sheets (Table 1). For each sputtering run, two polished Ti coupons ($25 \times 25 \times 2$ mm) have been fixed to the sample holder in equivalent positions relative to the Mo target maintaining a cathode–substrate distance of about 90 mm. Having two identical samples at a time means different analyses could be performed simultaneously.

The substrates were mechanically polished and cleaned using a standard procedure (ultrasonic cleaning in soap, ultrasonic rinsing in deionized water, final rinsing in acetone and ethanol). Mo film depositions were accomplished by sputtering a 2 inch polycrystalline molybdenum target (99.98%) with pure argon, krypton or xenon (all 99.9%) in a magnetron vacuum apparatus.

The substrate was rotated through a motorized automated system to promote the coating homogeneity and a constant bias voltage ($-40\ V_{DC}$) was applied to the growing film. A low substrate bias has been chosen: from preliminary results it is high enough to slightly improve the film quality (>adatom mobility) without increasing too much the film stress level and/or damaging the sample surface. The deposition duration has been set at 45 min to guarantee a *safety thickness*: it has to be sufficient to assure proper measurements of mechanical properties.

Table 1
Deposited molybdenum samples. Sample naming: 1, 2, 3 = series number; Ar, Kr, Xe = working gas; l (low pressure), m (middle pressure), h (high pressure) = 1.0×10^{-3}; 4.4×10^{-3}; 1.0×10^{-2} mbar respectively.

Sample	I(A)	P(W)	V(V)	Grain size (Å)	Microstructure FIB
Series 1 (I = cost)					
1-Ar-m	0.4	148	370	90	Columnar
1-Kr-m	0.4	147	370	55	Columnar
1-Xe-m	0.4	154	385	25	Porous
Series 2 (P = cost)					
2-Ar-l	0.30	149	497	260	Columnar
2-Ar-m	0.45	150	333	120	Columnar
2-Ar-h	0.56	150	268	80	Columnar
Series 3 (P = cost)					
3-Xe-l	0.23	150	652	106	Columnar
3-Xe-m	0.38	150	395	20	Porous
3-Xe-h	0.41	150	366	11	Porous

The working gas flux flow was finely regulated using a mass flow controller. Before filling the vacuum chamber with the sputtering gas, it was first pumped to a background pressure $\leq 1 \times 10^{-7}$ mbar. Prior to any deposition run, the Mo target was pre-sputtered for at least 5 min (using the same process parameters selected for the film deposition) maintaining the substrates isolated from the plasma by a shutter.

Argon, krypton or xenon was employed as the sputtering gas at three different pressures: 1.0×10^{-3} (l = low pressure), 4.4×10^{-3} (m = middle pressure) and 1.0×10^{-2} mbar (h = high pressure),[1] while all the deposited Mo films were obtained at a fixed power of ~150 W.

The effects of the deposition conditions on Mo films properties (morphology, crystal structure, grain size, hardness, elastic modulus, residual stress, adhesion) have been investigated.

Three different series of coatings were produced (Table 1). The first one (series 1) has been conceived to verify the importance of the working gas. Keeping unchanged all the other sputtering parameters, Ar, Kr and Xe have been used. The second and the third series of films have been thought to check the pressure effect. A few films have been deposited increasing progressively Ar (series 2) and Xe (series 3) working gas pressure without varying the power value (P = 150 W).

For series 1 constant current mode was selected. In this way it is possible to verify how deposition rate changes while modifying just the working gas mass. Then it was chosen to operate at constant power mode (series 2 and 3): it allows us to be sure not to heat the target too much (i.e. having a too high power level) when changing the pressure value.

2.2. Film characterization

2.2.1. Morphology and crystal structure

Film morphology was analyzed by a scanning electron microscope (Sigma FE-SEM, Carl Zeiss). The crystalline structure and orientation of the obtained coating were analyzed by X-ray diffraction (Philips PW 1830 diffractometer, Bragg–Brentano geometry, CuKα). Crystallographic parameters were evaluated using MAUD (Material Analysis Using Diffraction) [21,22], a program based on the Rietveld refinement method [23].

2.2.2. Mechanical properties and average residual stress

Elastic modulus (E) and hardness (H) of Mo coatings were measured by instrumented nano-indentation testing, using an Agilent G200 nano-indenter. Tests were made by using the continuous stiffness measurement (CSM) mode, which allows obtaining H and E as a continuous function of depth from a single indentation experiment. Tests were performed with a frequency of 45 Hz, amplitude of oscillation 2 nm, constant strain rate of 0.05 s^{-1}, and maximum penetration depth 1000 nm while reasonable values from literature were assumed for the Poisson's ratios and the elastic modulus of both substrate and film [24,25]. Results of hardness and modulus profiles are reported after averaging over 20 different tests within the depth range of 100–120 nm.

The coating's residual stress state was analyzed by using the focused ion beam (FIB) micro-scale incremental ring-core method, a material removal method that was recently proposed for local residual stress measurement with sub-micrometer spatial resolution [26]. The procedure consists of FIB milling of a micron-size annular trench of increasing depth, combined with high-resolution in-situ scanning electron

[1] This is just a simplification. It will be clear in the following it is possible to define *low*, *middle* and *high* pressure just after specifying the working gas mass (same target material).