Size effects on the mechanical behavior of nanometric W/Cu multilayers

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Résumé :

Le comportement mécanique de multicouches W/Cu nano structurées préparées par pulvérisation ionique a été analysé en utilisant une méthode combinant la diffraction des rayons X et la déformation in situ. Les essais on été réalisés sur une source de lumière synchrotron pour analyser la réponse élastique du tungstène. Trois différentes microstructures on été analysées : l'échantillon composé de la couche de tungstène la plus fine présente un comportement mécanique différent de celui attendu pour un matériau massif. Néanmoins, des mesures par microscopie électronique en transmission (MET) et par diffusion centrale en incidence rasante (GISAXS en anglais) révèlent des discontinuités dans les sous-couches de cuivre. Comme les déformations de ces clusters de cuivre et les contributions des joints de grain ne sont pas expérimentalement accessibles, une approche par simulation atomistique devient indispensable.

Abstract :

The mechanical behavior of nanostructured W/Cu composites prepared by ion beam sputtering has been investigated using a method combining X-ray diffraction and tensile testing. Tests were performed on a synchrotron light source to analyze the elastic response of the tungsten phase. Three different microstructures have been analyzed: the specimen composed of the thinner tungsten layers reveals an elastic behavior different from the one expected assuming bulk elastic constants. However, Transmission Electron Microscopy (TEM) and Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) measurements reveal discontinuities in the copper layers. As the strain in the related copper clusters as well grains boundary contributions are not experimentally accessible, atomistic calculation are of utmost importance.

Mots clefs: multicouches métalliques, déformation in situ, diffraction des rayons X, effets de taille, élasticité

1 Introduction

Nanometer scaled materials meet non negligible surface contribution yielding deviations from mechanical bulk materials behavior. Stratified samples have attracted much attention since one dimension can be tailored down to the nano-scale, leading to novel electronic, magnetic, optical and mechanical applications. Despite the number of studies devoted to length scale dependence of strength and deformation mechanisms in nano-scale multilayers [1-6], few of these focus on the mechanical response in the elastic domain. Elastic constants analysis in nano-crystalline metallic thin films and multilayers by means of a method combining X-ray diffraction and tensile testing has been a constant challenge in our laboratory for several years [7-10]. The present paper focuses on experiments involving stratified W/Cu samples with tungsten layer thicknesses ranging from 10.8 nm down to 1.5 nm and presenting constant average copper layer thickness of 0.2 nm. X-ray measurements were performed at the European Synchrotron Radiation Facility (Grenoble, France).

2 Experiments

2.1 Specimen preparation

W/Cu multilayers were deposited by ion-beam sputtering in a NORDIKO 3000 device at room temperature, tungsten being the first deposited layer, on 127.5 μm thick polyimide (Kapton®) dogbone foils and on 200 µm and 600 µm thick naturally oxidized Si (001) wafers. The gauge part of dogbone samples has a size of 6 × 15 mm². Sample characteristic data, including the number of (W,Cu) layer pairs and the total film thickness of each specimen, are given in Table I. The film mean residual stresses were evaluated using the curvature method with the dedicated 200 µm Si cantilevers. The global stress states set in thin films were strongly compressive. X-ray diffraction pole figures measurements showed that W layers exhibit both <110> and <111> fiber-texture [11]. X-ray reflectometry measurements combined with atomic concentration determined by EDX (Energy dispersive X-ray) allowed us to establish effective thicknesses shown in Table I.

Sample designation	Effective thicknesses			Number of (W,Cu) layer pairs	Total film thicknesses	Residual stresses	
	Λ (nm)	t_W (nm)	t_{Cu} (nm)		(nm)	Film (GPa)	W layers (GPa)
W/Cu 10.8/0.2	11.0	10.8	0.2	15	174	-2.8	-5.3
W/Cu 2.8/0.2	3.0	2.8	0.2	60	198	-3.2	-5.8
W/Cu 1.5/0.2	1.7	1.5	0.2	100	185	-3.2	-6.8

Table I: Specifications of W/Cu samples submitted to in situ tensile tests at ESRF BM02 beamline. The uncertainties on thicknesses and stresses are about 5% and 10% respectively.

However, Transmission Electron Microscopy (TEM) (Fig. 1) and recent Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) [12] investigations have revealed that copper layer may be discontinuous. Thus, W/Cu composites are not exactly multilayers but tungsten matrix containing periodic copper dispersoïd layers.

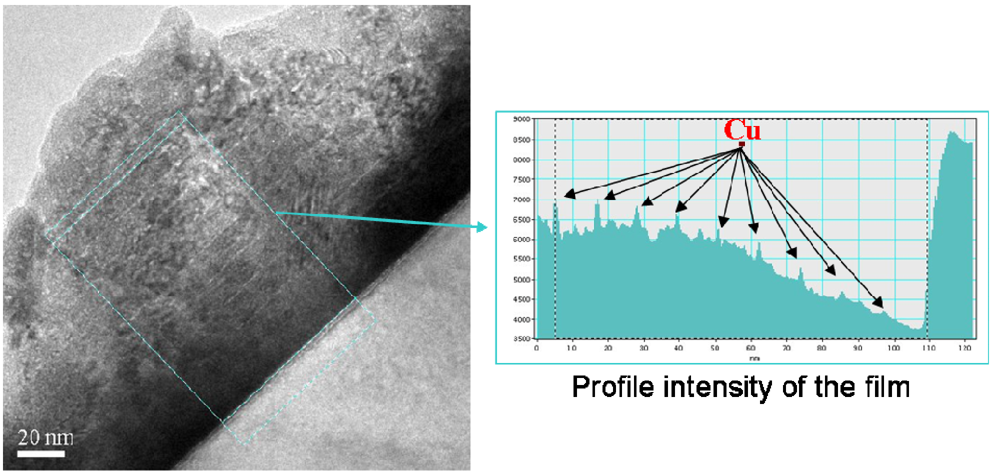

Figure 1: TEM Bright Field realized on W/Cu 10.8/0.2 showing the thin film stratification and suggesting copper layer discontinuities (confirmed by GISAXS).

2.2 Tensile testing and X-ray diffraction

Combined tensile tests and XRD measurements were realized in a seven-circle diffractometer at the BM02 beam line of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). A 200 N Deben™ mini-tensile testing device allows performing in situ tensile tests and can be equipped with several load cells (capacity from 5 N to 200 N) according to the chosen force range investigated [7].

The measurement of lattice strains by X-ray diffraction enables to determine the applied or residual strains in crystalline materials. The lattice strain is measured along a direction which is defined with respect to the sample geometry by the angles φ and ψ defined in Fig. 2.

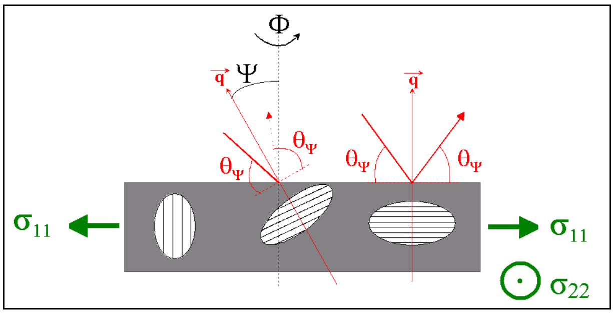

Figure 2: XRD Geometry: ψ is the angle between the surface normal of the sample and the measuring direction, i.e. the normal to the diffracting planes, and φ is the azimuth, i.e. the rotation angle around the normal to the sample surface.

The technique based on the well-known "$\sin^2\psi$ method" [13-14] consists in applying a uniaxial tensile force to the film/substrate sample and monitoring the shift of one or several {hkl} peak positions. The applied force is recorded via the load cell supplied on the tensile tester. The elastic strain of tungsten phase is obtained by X-ray measurement of the lattice plane distance defined by:

$$\varepsilon_{\varphi,\psi} = \ln\left(\frac{d_{hkl}}{d_{hkl}^{ref}}\right) \tag{1}$$

where d_{hkl} is the lattice plane distance in tungsten layers when the specimen is submitted to the global force F along the tensile axis, and d_{hkl}^{ref} the value of this distance in the reference load state along the same direction defined by (ψ , φ).

The ψ values were chosen with respect to preferred crystallographic orientations set in the layers of each sample, that is <110> and <111> fiber-textured for W layers of dispersoïd composites. Due to the low copper X-ray scattering factor and deposited copper quantities, no diffracting information can be extracted from copper dispersoïd layers. Improved jaws have been used to guarantee specimen flatness during loading which greatly reduced uncertainties.

These measurements dedicated to tungsten elastic constant determination have been performed with numerous load steps ranging from 1.5 N to 17 N. The whole load range was supposed to be included in the sample elastic strain domain (according to prior laboratory tests). It should be noted that these measurements would not have been possible with a conventional laboratory X-ray source, even with very long acquisition times, since uncertainties are of the same order as the peak shifts; here the X-ray synchrotron source allows performing good quality measurements, with a rather high dynamic, in a quite short recording time (around 2 hours for each loading step).

3 Results and discussion

Results are focused on W-{310} strain measured on W/Cu 1.5/0.2. Interfaces between the substrate and the first tungsten layer and between all W and Cu sub-layers (considered as continuous layers for calculation, in a first approximation) are assumed to be perfect, i.e. the strain is transmitted unchanged through interfaces. In this case, by neglecting the edge effects, a biaxial stress state can be assumed ($\sigma_{33} = 0$, axis n°3 being the normal to the specimen surface). Considering bulk elastic constants, it is thus possible to evaluate effective stress applied to tungsten sub-layers and the strain induced from increment load supported by film/substrate sample (using bulk elastic constants). Hooke's law allows estimating the strain expected in W layers for each value of the applied force by means of equation 2:

$$\varepsilon^{W}_{\varphi=0°,\psi} = \left(\frac{1+\nu_W}{E_W}\sigma^W_{11} - \frac{\nu_W}{E}\left(\sigma^W_{11} + \sigma^W_{22}\right) \right)\sin^2\psi - \frac{\nu_W}{E_W}\left(\sigma^W_{11} + \sigma^W_{22}\right) \tag{2}$$

where E_W and ν_W refer to the Young's modulus and Poisson's ratio of tungsten layers, $\sigma_{11}{}^W$ is the stress in W layers along the tensile axis (longitudinal stress) and $\sigma_{22}{}^W$ the stress along the perpendicular axis (transversal stress).

Applied stress along tensile direction ($\sigma_{11}{}^W$) and induced stress along the perpendicular direction ($\sigma_{22}{}^W$) can be calculated as follows:

$$\sigma^W_{11} = \frac{A_W B_W \sigma^{tot}}{B_W{}^2 - C_W{}^2} \quad \text{and} \quad \sigma^W_{22} = \frac{-A_W C_W \sigma^{tot}}{B_W{}^2 - C_W{}^2}$$

$$\text{with} \begin{cases} A_W = E_W\left(1-\nu_K^2\right)\left(1-\nu_{Cu}^2\right) \\ B_W = \left[E_K f_K\left(1-\nu_{Cu}^2\right)\left(1-\nu_K\nu_W\right) + E_{Cu} f_{Cu}\left(1-\nu_K^2\right)\left(1-\nu_{Cu}\nu_W\right) + E_W f_W\left(1-\nu_{Cu}^2\right)\left(1-\nu_K^2\right)\right] \\ C_W = \left[E_K f_K\left(1-\nu_{Cu}^2\right)\left(\nu_K - \nu_W\right) + E_{Cu} f_{Cu}\left(1-\nu_K^2\right)\left(\nu_{Cu} - \nu_W\right)\right] \end{cases} \tag{3}$$

where f_K, f_W, and f_{Cu} are the volume fractions of the Kapton® substrate, tungsten layers and copper layers, respectively; E_K, ν_K, E_{Cu}, ν_{Cu} refer to the Young's moduli and Poisson's ratios of the substrate, and copper layers, respectively; σ^{tot} represents the total applied stress, i.e. F/S, S being the specimen transversal section. Experimentally determined values (E_K = 5 GPa, ν_K = 0.34) were employed for the Kapton® substrate while bulk polycrystalline Poisson's ratios (ν_W = 0.28 and ν_{Cu} = 0.343) were considered.

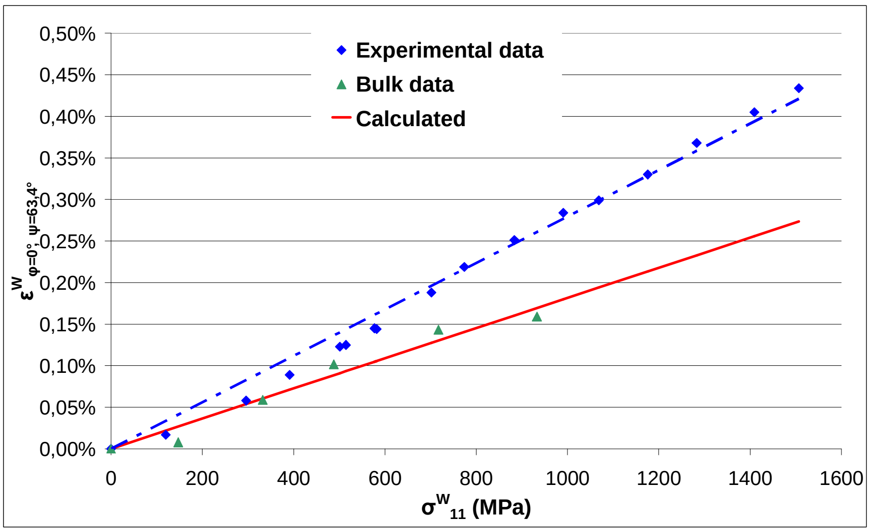

Figure 3: Strain deduced from the shift of the W(310) diffraction peak measurements ♦ as a function of estimated applied stress increment (the first loaded state being chosen as the reference state) in W layers along the loading axis, for ψ = 63.4° and φ = 0°, for the thinnest W layer thickness. (λ_{XR} = 0.127 nm). The dotted line represents the linear regression obtained from experimental data while the continuous line is calculated from equations (2) and (3) considering bulk elastic constants. The straight red line fits well the elastic strain ▲ measured on a 200-nm-thick tungsten layer (performed with similar deposition conditions) following W(211) diffracting plane (ψ = 61.9° and φ = 0°).

X-ray measurements allow thus determining strain associated to each loading increment (first loading state taken as a reference) as a function of the applied stress along the tensile direction. Figure 3 shows the strain determined from W-{310} diffraction peak shift along a particular direction defined by φ = 0° (corresponding to the tensile direction) and ψ = 63.4°. These experimental data concern the W/Cu periodic dispersoïd composite presenting the thinnest W layer thickness, i. e. W/Cu 1.5/0.2. As shown in figure 3, the experimental strain obtained deviated from that calculated using bulk elastic constants (continuous line). Instead, the bulk calculated response predicts well the experimental data obtained on a thick (200 nm) W layer. We observe that the (ε, σ) slope value is much more important for the nanostructured layer than for 'bulk' materials. The elastic softening of W layers may be explained by a size effect. Indeed, the grain size being only about 1.5 nm, a large part of atoms is located close to a surface, an interface or a grain boundary. However, we have to keep in mind that the interface roughness or even mixing effect may also contribute to this variation.

4 Concluding remarks

Elastic strain measurements have been realized using a method combining X-ray diffraction and tensile testing. High accuracy X-ray strain measurements are essential for the determination of elastic constants since the strain range is limited (a few tenths of percent). Moreover, the diffracting volume in polycrystalline thin films can be very small and the photon energy has to be tunable to avoid peak overlapping for multiphase materials. For all these reasons, performing tensile tests with a high precision goniometer at a synchrotron beam line is essential. Preliminary results obtained monitoring W-{310} diffraction peak shift on W/Cu 1.5/0.2 sample clearly show a size effect on the mechanical response. Indeed, nanostructured tungsten layers elastic response strongly differs from the one expected for a bulk material. This might be attributed to an elastic constant softening for a 1.5 nm tungsten grain size. However, further analysis is needed to confirm such a tendency and particularly, the mechanical influence of copper inclusions. Indeed, composite systems containing two materials with different mechanical properties present a complex mechanical behavior since their elastic strain domains and ductility are different. So far, monitoring the strains in both elements during tensile tests is not possible in such samples. In order to understand in detail the causes of elastic constant softening, our team develops atomistic simulations. Simulated tensile testing of self-supported single-crystal film of W have revealed a Young's modulus softening coupled with a strengthening of the Poisson's ratio. This effect becomes larger when monocrystalline layer thickness decreases under 2 nm [15]. These first results are qualitatively consistent with experimental measurements. However, in order to corroborate X-ray experiments, it is imperative to realize atomistic calculations on polycrystals. This is done using the Voronoi method for building polycrystals. It allows to realize bulk tungsten polycrystals with different grain size, preliminary step before modeling model polycrystalline thin films. The objective will be thus to study the elastic response of a layered polycrystalline W/Cu composite, by atomistic simulation. Eventually, it will provide a better understanding of the influence of discontinuous copper layers on the mechanical behavior.

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