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# **X-ray Diffraction Study of the Mechanical Elastic Properties of Nanometric W/Cu Multilayers**

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## **ABSTRACT**

The mechanical behavior of W/Cu multilayers with a period of 24 nm and a 1/3 W/Cu thickness ratio prepared by magnetron sputtering was analyzed using a method combining X-ray diffraction and tensile testing. Tests were performed both with a conventional and a synchrotron light source to analyze the elastic response of the system. Comparison between the strain-load curves obtained in both experimental conditions and estimated curves clearly shows that high quality synchrotron measurements are a preliminary condition for size-effect studies. Moreover, cyclic tests were used to determine the elastic domain of each material and compare their mechanical responses. Plastic strain was observed in copper before in tungsten layers in accordance with the mechanical behavior of their bulk counterparts.

## **INTRODUCTION**

In thin films or multilayers with nanometer thickness, the contribution of atoms located in surface regions and grain boundaries becomes non negligible resulting in deviations from the mechanical behavior of bulk materials. Multilayers have attracted much attention since one dimension can be tailored down to the nano-scale, leading to novel electronic, magnetic, optical and mechanical applications. A lot of studies have been devoted to experimental determination of the length scale dependence of strength and also to the theory and modeling of deformation mechanisms in nano-scale multilayers [1-6]. However the mechanical response of such materials has little been studied in the elastic domain.

Analyzing elastic constants 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]. In the present paper, we will focus on experiments on W/Cu multilayers with a 24 nm period and a 1/3 W/Cu thickness ratio performed both in our laboratory and at the European Synchrotron Radiation Facility (Grenoble, France). The benefit from using synchrotron X-ray sources for sufficient accuracy in these experiments will be evidenced. A comparative study of the evolution of strains in tungsten and copper during cyclic tensile tests will also be presented.

## EXPERIMENTS

### Specimen preparation

W/Cu multilayers were deposited either in a magnetron sputtering chamber or in an ion-beam sputtering NORDIKO 3000 device at room temperature, tungsten being the first deposited layer, on 127.5  $\mu\text{m}$  thick polyimide (Kapton<sup>®</sup>) dogbone foils for tensile tests and on 200  $\mu\text{m}$  and 600  $\mu\text{m}$  thick naturally oxidized Si (001) wafers for characterization measurements. The gauge part of dogbone samples has a size of 6  $\times$  15 mm. The nominal value of the multilayer period  $\Lambda$  was 24 nm with a 1/3 thickness ratio of tungsten and copper (i.e. 6 nm W and 18 nm Cu). This ratio was chosen to compensate for the lower X-ray atomic scattering factor of copper, and thus to obtain a diffraction signal of copper similar to the one of tungsten. The number of (W,Cu) layer pairs and the total film thickness of each tensile-testing specimen are given in Table I. Small angle X-ray diffraction measurements allowed us to determine the actual value of the thickness period. The mean residual stresses in the multilayers were evaluated using the curvature method with the dedicated 200  $\mu\text{m}$  thick Si cantilevers. The global stress state was slightly tensile ( $\sim$  200 MPa) in the magnetron sputtered layers and strongly compressive in the ion-beam sputtered ones ( $\sim$  -1 GPa). X-ray diffraction rocking-curves measurements showed that W and Cu layers were  $\langle 110 \rangle$  and  $\langle 111 \rangle$  fiber-textured, respectively.

**Table I** : Experimental conditions and specimen specifications for in situ tensile tests performed on W6/Cu18 multilayers in our laboratory and at ESRF BM02 beam line.

In situ tensile test	ESRF BM02	Laboratory	
Load range	<i>Elastic range test:</i> 0 $\rightarrow$ 8 N	<i>Elastic range test:</i> 0 $\rightarrow$ 8 N	<i>Cyclic test:</i> 1 <sup>st</sup> loading: 0 $\rightarrow$ 9.5 N 2 <sup>nd</sup> loading: 0.5 $\rightarrow$ 23.6 N 3 <sup>rd</sup> loading: 10.4 $\rightarrow$ 36.5 N 4 <sup>th</sup> loading: 11.5 $\rightarrow$ 57 N Final unloading: $\rightarrow$ 24.2 N
X-ray wavelength	0.1387 nm	0.154 nm (conventional Cu X-ray tube)	
Diffraction lines	W(310) ( $2\theta \approx 87^\circ$ )	W(110) ( $2\theta \approx 40^\circ$ )	W(110) ( $2\theta \approx 40^\circ$ ) Cu(200) ( $2\theta \approx 50^\circ$ )
Sputtering mode	Magnetron	Magnetron	Ion-beam
Total thickness (nm)	1024	1054	213
Number of W/Cu pair	45	45	10
Effective period (nm)	22.75	23.45	21.1
Mean residual stresses (GPa)	0.25	0.14	- 1.0

### Tensile testing and X-ray diffraction

Combined tensile tests and XRD measurements were realized both at the BM02 beam line of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) and in our laboratory on a Seifert four-circle diffractometer. A 200 N Deben<sup>TM</sup> mini-tensile testing device allows performing in situ tensile tests on most XRD goniometers [7]. According to the chosen force range, a 20 N and a 200 N load cells were used.

The technique used here is based on the well known “ $\sin^2\psi$  method” [11-12]; it consists in applying a uniaxial tensile force to the multilayer/substrate set and monitoring the shift of one or several {hkl} peak positions as a function of  $\sin^2\psi$  ( $\psi$  being the angle between the diffracting planes and the normal to the sample surface) and of the applied force. The global applied load is recorded via a load cell. X-ray measurements on W and Cu reflections allow us to determine the average elastic strains in each type of layers. The measurements meant to determine elastic constants of tungsten and copper sub-layers have been performed with numerous load steps in a small load range. Moreover, four tensile loading/unloading cycles with increasing upper load have been done in our laboratory in order to compare the mechanical response of tungsten and copper in a wide strain range, evidencing the apparition of plastic flow and even rupture. The detailed experimental conditions for these tensile tests are given in Table I.

## RESULTS AND DISCUSSION

### Elastic strain domain

Since analysis of ESRF measurements are still under progress, we will focus on results concerning tungsten. Figure 1 shows the evolution of the strain measured in a particular ( $\phi, \psi$ ) direction ( $\phi = 0$  corresponding to the tensile direction and  $\psi \approx 63^\circ$ ) using the shift of a tungsten diffraction peak (110 or 310). In-grain strain is defined by

$$\varepsilon_{0,\psi} = \ln\left(\frac{d(F)}{d_{ref}}\right), \quad (1)$$

$d(F)$  being the (hkl) interreticular distance in tungsten layers when the specimen is submitted to the global force  $F$  along axis no.1 , and  $d_{ref}$  the value of this distance in the reference load state, for  $\phi=0$  and a given  $\psi$  value.

We assume a biaxial stress state ( $\sigma_{33} = 0$ , axis no.3 being the normal to the specimen surface) and perfect interfaces between the substrate and the first tungsten layer, and between all W and Cu sub-layers. The strain expected in W layers for each value of the applied force can be estimated by means of equation 2:

$$\varepsilon_{0,\psi}^W = \left( \frac{1+\nu_W}{E_W} \sigma_{11}^W - \frac{\nu_W}{E} (\sigma_{11}^W + \sigma_{22}^W) \right) \sin^2 \psi - \frac{\nu_W}{E_W} (\sigma_{11}^W + \sigma_{22}^W) \quad (2)$$

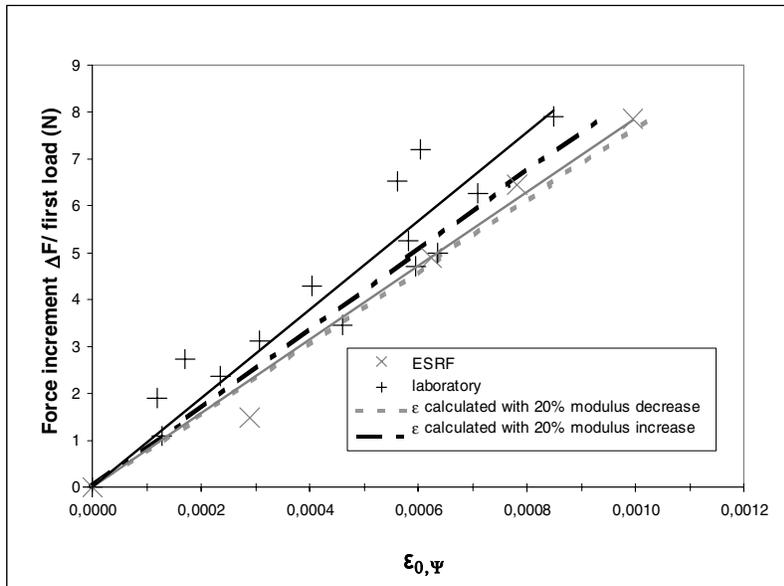
$E_W$  and  $\nu_W$  refer to the Young's modulus and Poisson's ratio of tungsten layers;  $\sigma_{11}^W$  is the stress in W layers along the tensile axis (longitudinal stress) and  $\sigma_{22}^W$  the stress along the perpendicular axis (transversal stress).  $\sigma_{11}^W$  and  $\sigma_{22}^W$  can be calculated as follows:

$$\sigma_{11}^W = \frac{A_W B_W \sigma^{tot}}{B_W^2 - C_W^2} \quad \text{and} \quad \sigma_{22}^W = \frac{-A_W C_W \sigma^{tot}}{B_W^2 - C_W^2} \quad (3)$$

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

where  $f_K$ ,  $f_W$ , and  $f_{Cu}$  are the volume fractions of the Kapton® substrate, tungsten layers and copper layers, respectively;  $E_K$ ,  $\nu_K$ ,  $E_{Cu}$ ,  $\nu_{Cu}$  refer to the Young's modulus and Poisson's ratio of the substrate, and copper layers, respectively.  $\sigma_{tot}$  represents the average applied stress, i.e.  $F/S$ ,  $S$  being the specimen transversal section. Previously measured values ( $E_K = 5.5$  GPa,  $\nu_K = 0.29$ ) were employed for the Kapton® substrate; bulk polycrystalline values were used for  $\nu_W$  (0.28) and  $\nu_{Cu}$  (0.343); for  $E_W$  and  $E_{Cu}$ , a possible reduction or increase of 20% compared to literature bulk values (411 GPa for W and 130 GPa for Cu) was considered to define upper and lower limits. These calculated strains are symbolized by the dotted curves on figure 1.

A high scattering of experimental values is observed in the case of laboratory measurements. In fact, stress-induced peak shifts are very small (a few hundredths of degree) in the  $2\theta$  range used here resulting in poor accuracy for the determination of strains. However, higher index peaks presented a too low signal-on-noise ratio. Thanks to the high quality and intensity of synchrotron X-ray beam, the measurements could be performed at higher  $2\theta$  values. It clearly appears on figure 1 that strain values are less scattered. Furthermore, the slope of the  $(\epsilon, F)$  curve is approximately equal to the average estimated value; this result corroborates the assumption that no size effect appears for such a large multilayer period (24 nm). In fact, size effects on the elastic behavior of nano-sized materials reported so far do not exceed 20% variations of elastic coefficients with respect to bulk references [3, 13-14]. Consequently, considering the impact on strains of a 20% variation of Young's modulus, it does not seem possible to evidence a size effect on elastic constants without high precision strain measurements at a synchrotron beam-line.



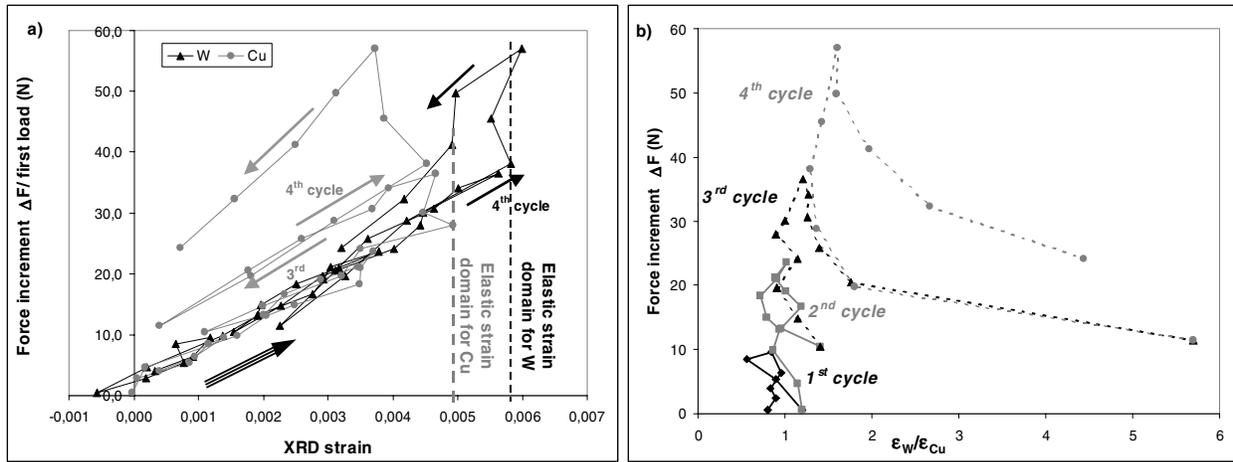
**Figure 1:** Load increment applied to the film/substrate set versus the elastic strain in the tungsten sublayers of W/Cu multilayers, measured in the  $\psi = 63^\circ$  direction. Two experiments are compared: a laboratory one and an ESRF one. Straight lines represent the linear regression on experimental data. Dotted lines correspond to the strain in W calculated under the hypothesis of a 20% Young's modulus increase or decrease with respect to bulk values.

### Plastic strain domain

In order to better characterize the mechanical response of W/Cu multilayers both in the elastic and plastic range up to rupture, four tensile loading/unloading cycles with increasing upper load were performed in our laboratory. The evolution of elastic strains in each material was monitored via the shift of one diffraction peak for an as high as possible value of the  $\psi$

angle; the chosen values,  $60^\circ$  for W and  $54.7^\circ$  for Cu, correspond to pole directions of the fiber-textured layers. Figure 2a presents the elastic strains in W and Cu for these  $\psi$  values while figure 2b shows the evolution of the strain ratio  $\varepsilon_W/\varepsilon_{Cu}$ .

It clearly appears on figure 2a that strains are reversible in both tungsten and copper in the two first loading/unloading cycles. Then, the elastic strain saturates in copper during the third loading stage ( $F > 25\text{N}$ ) and finally in tungsten during the fourth loading stage ( $F > 35\text{N}$ ). The saturation of the elastic strain corresponds to the onset of plastic yield in each type of layers and then the elastic strain range is larger for tungsten than for copper. The slopes of unloading curves are constant for the first three unloads and significantly smaller in the last one. This observation may be accounted for by plastic deformation in W when the applied tensile force exceeds 35 N. However in a previous work [9], such behavior of tungsten layers was attributed to the appearance of cracks in W/Cu multilayers with equal thickness of W and Cu. The divergence of the W/Cu strain ratio observed during the 3<sup>rd</sup> and 4<sup>th</sup> unloading stages on figure 2b corroborates this interpretation: plastic strain appears in copper layers while tungsten layers are still elastically deformed until  $F \sim 35\text{N}$ ; then the residual lengthening in Cu limits elastic contraction in W during unloading stages. It should be noted that the high level of compressive residual stresses in the as-deposited multilayers may account for the large extend of the linear deformation domain observed here.



**Figure 2:** Evolution of a) the total force increment applied to the film/substrate set as a function of X-ray elastic strains measured in tungsten and copper for a particular  $\psi$  value ( $\psi_W = 60^\circ$ ,  $\psi_{Cu} = 54.7^\circ$ ), and b) the force increment as a function of the ratio of W strain on Cu strain. Dotted lines on figure 2a indicate the observed elastic strain domain upper limit.

Since the onset of plastic yield should depend on the layer thickness in the nanometer range, such experiments are essential to delimit the linear elastic strain domain for each type of multilayer before performing precise measurements in a restricted strain range for the determination of elastic coefficients.

## CONCLUSIONS

High accuracy X-ray strain measurements are essential for the determination of elastic constants in thin films since the strain range is limited (a few tenths of percent). For this reason, performing tensile tests with a high precision goniometer at a synchrotron beam line is essential.

Composite systems containing two materials with different mechanical properties present a complex mechanical behavior since their elastic strain domains and ductility are different. Monitoring the strains in both elements of the multilayer during tensile tests allow to characterize their elastic domain and the influence of the response of each one on the other. By means of cyclic tensile tests in the case of a 24 nm period W/Cu multilayer, we have shown that copper plastic flow first appears and thus limits the elastic unloading of tungsten; at higher applied stress level, plastic flow also appears in tungsten layers leading to the saturation of the measured elastic strain and to deep modifications of the multilayer mechanical response.

Further experiments of the same type will be performed on synchrotron beam lines to analyze the behavior of smaller period multilayers taking into account the elastic interaction between grains [15] in case of elastic anisotropy (copper for instance) and increasing the atomic scattering factor of the anisotropic layer by changing copper for gold, this last element being extensively studied in our group [10, 15-16].

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