



**HAL**  
open science

## Size effect on intragranular elastic constants in thin tungsten films

P. Villain, Ph. Goudeau, P.-O. Renault, K. Badawi

► **To cite this version:**

P. Villain, Ph. Goudeau, P.-O. Renault, K. Badawi. Size effect on intragranular elastic constants in thin tungsten films. *Applied Physics Letters*, 2002, 81 (23), pp.4365-4367. 10.1063/1.1527229 . hal-03703017

**HAL Id: hal-03703017**

**<https://hal.science/hal-03703017>**

Submitted on 24 Jun 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Size effect on intragranular elastic constants in thin tungsten films

P. Villain,<sup>a)</sup> Ph. Goudeau, P.-O. Renault, K.F. Badawi

*Laboratoire de Métallurgie Physique, UMR 6630 CNRS/Université de Poitiers, SP2MI, BP 30179, 86962 Futuroscope Chasseneuil cedex, France*

### **Abstract:**

The size effect on the elastic constants of nanocrystalline tungsten has been investigated in the case of W/Cu multilayers with two modulation wavelengths (3.1 and 24.0 nm). Tungsten Young's modulus and Poisson's ratio have been measured thanks to a technique coupling x-ray diffraction with *in situ* tensile testing. It is demonstrated that the in-grain thin film elastic constants are highly microstructure – sensitive: in the “3.1 nm” multilayer, tungsten Poisson's ratio is larger than the bulk one while it is smaller in the “24.0 nm” multilayer; a softening of tungsten Young's modulus is evidenced in the case of the specimen with the smallest period.

Author to whom correspondence should be addressed; electronic mail: [pascale.villain@univ-poitiers.fr](mailto:pascale.villain@univ-poitiers.fr)

Theoretical studies concerning nanocrystalline materials<sup>1,2</sup> predict noticeable modifications of their elastic properties compared to the bulk ones due to a high volume proportion of surface and interface atoms, as well as a high point defect density. Grain boundaries, free surfaces and interfaces induce important alterations of cohesion energies. Numerous experimental studies have evidenced a very probable softening of elastic constants in nanostructured materials, in particular the  $C_{44}$  stiffness coefficient in multilayers with very low modulation wavelength ( $\Lambda \leq 3$  nm)<sup>3,4,5</sup>. In previous papers, we described an experimental technique combining *in situ* tensile testing and x-ray diffraction to extract the Poisson's ratio<sup>6</sup> and the Young's modulus<sup>7</sup> of supported thin metallic films and multilayers. This diffractometric method differs from all the other mechanical, vibration, and acoustic techniques since it allows to measure average **in-grain** strains, and thus intragranular elastic constants.

This letter deals with the study of the evolution of tungsten intragranular elastic constants in W/Cu multilayers as a function of the modulation wavelength  $\Lambda$ . This system was chosen for the following experimental and physical considerations: copper and tungsten are not miscible, tungsten presents a high atomic scattering factor and is elastically isotropic, a lot of structural studies have already been done on this system<sup>8,9</sup>.

The technique used here, based on the well known “ $\sin^2\psi$  method”<sup>10,11</sup>, consists of applying a uniaxial tensile force to the film/substrate system, *in situ* in an x-ray diffractometer. The formalism is very simple in the case of a polycrystalline elastically isotropic material such as tungsten: a linear relation is expected between the shift of each  $\{hkl\}$  peak position and  $\sin^2\psi$ ,  $\psi$  being the angle between the normal to the diffracting planes and the normal to the sample surface. For each applied load value, the  $\sin^2\psi$  curves are determined for the tungsten layers. The slope  $P_1$ , on the one hand, and the intercept  $m_1$ , on the other hand, of the linear regressions on these experimental data is plotted as a function of the applied load  $F$ . Assuming an uniaxial applied stress state (similar Poisson's ratios for the film and the substrate), the mean Young's modulus  $E_w$  of tungsten sublayers can be then calculated by means of the following relation:

$$E_W = \frac{1}{t_W} \left( \frac{1}{b(P^* + m^*)} - E_s t_s - E_{Cu} t_{Cu} \right) \quad (1)$$

where  $b$  is the sample width,  $t_s$  the substrate thickness,  $t_W$  (resp.  $t_{Cu}$ ) the total thickness of the W (resp. Cu) sublayers,  $E_s$  (resp.  $E_{Cu}$ ) the substrate (resp. copper) Young's modulus,  $P^*$  (resp.  $m^*$ ) the slope of the  $(P_1, F)$  linear curve (resp. the  $(m_1, F)$  curve).

The mean Poisson's ratio  $\nu_W$  of tungsten sublayers is simply deduced from a combination of  $P^*$  and  $m^*$ :

$$\nu_W = -\frac{m^*}{P^* + m^*}. \quad (2)$$

It is worth noting that the determination of  $\nu_W$  does not need any numerical value concerning geometrical nor mechanical properties of the various parts of the system. For the Young's modulus measurement, the substrate Young's modulus and the copper one must be known, as well as the respective thickness of the three constituents.

W/Cu multilayers were deposited onto a 127.5  $\mu\text{m}$  thick polyimide (Kapton<sup>®</sup>) dogbone substrate by ion beam sputtering at room temperature, tungsten being the first deposited layer. The in-plane sample dimensions were  $8 \times 3 \text{ mm}^2$ . The total thin film thickness ranged from 220 to 240 nm. Before performing the *in situ* tensile tests, several characterization experiments have been done. X-ray reflectivity measurements were performed in our laboratory to deduce the modulation wavelength  $\Lambda$  (thickness of one W/Cu bilayer) from the small angle Bragg's peak positions. Atomic proportions of tungsten and copper were determined thanks to Electron Dispersive X-ray Spectroscopy (EDXS) measurements. The mean thickness of tungsten ( $e_W$ ) and copper ( $e_{Cu}$ ) individual sublayers was deduced from  $\Lambda$  and the atomic proportions, assuming the density of each material is equal to the bulk one<sup>12</sup>. All these values are reported in Table I for the two specimens studied here ( $\Lambda = 3.1 \text{ nm}$  and  $\Lambda = 24.0 \text{ nm}$ ). It should be noticed that nanostructured copper and tungsten sublayers may be less dense than the bulk materials as the modulation wavelength  $\Lambda$

decreases. This effect implies small variations on the  $e_{Cu}$  and  $e_W$  values when considering the density ratio of both elements in the thickness calculation and thus slightly influences the precision on the modulus measurement (Eq. (1)).

The initial microstructural and mechanical state was also characterized. Residual stresses ( $\sigma_{XRD}$ ) and stress-free lattice parameters ( $a_0$ ) of the tungsten sublayers were analyzed by x-ray diffraction; results are given in Table I. It can be seen that tungsten is in a strongly compressive stress state; the  $\sigma_R$  value increases with  $\Lambda$ . In the small period multilayer, the stress-free lattice parameter is smaller than the bulk one ( $a_{bulk} = 0.3165 \text{ nm}$ <sup>12</sup>) whereas it is larger in the other specimen. This observation reveals important differences in the microstructure of these two specimens: a vacancy-type structure and a columnar grain morphology with nanometer-sized intergranular voids when the sublayers are the thinner, a densified structure with interstitial incorporation when the sublayer thickness increases. This can be related to the growth mode: transition from an initial discrete-island stage towards a continuous film via an island coalescence process<sup>13</sup>. Comparing the x-ray residual stresses with the residual stress values obtained by the substrate curvature method ( $\sigma_{curvature}$  in Table I), it can be seen that the mean stresses in the whole thin films are considerably lower than the in-grain stresses in tungsten sublayers. This can be accounted for by the mechanical contribution of interfaces and copper layers in the total thin film stress: previous studies have demonstrated that copper layers are almost stress-free<sup>14</sup>.

The *in situ* tensile tests were performed at the French synchrotron radiation facility L.U.R.E. (Orsay, France) on the H10 and DW22 beam lines where we took advantage of the high x-ray beam intensity and quality, as well as the large wavelength range accessible. For each specimen, several increasing strains were applied and x-ray diffraction measurements were realized in each case. Table II presents examples of applied force values and corresponding in-grain elastic strains ( $\epsilon_{11}^A$ ) in the tungsten layers deduced from x-ray measurements<sup>15</sup>. The calculation of  $\epsilon_{11}^A$  allows to control that the applied strain remains in the elastic domain. In Fig.1, the evolution of the slope  $P_1$  and the

intercept  $m_1$  of the  $\sin^2\psi$  curves are plotted versus the mean applied stress  $\sigma_m = F/S_{tot}$ , where  $S_{tot}$  is the section area of the sample ( $S_{tot} = (t_s + t_w + t_{Cu}) \times b$ ). The slopes of these curves are clearly different for the two multilayers. Linear regressions on the experimental data give the values of  $P^*$  and  $m^*$  for each specimen; we can then calculate tungsten Young's modulus and Poisson's ratio via Eq. (1) and Eq. (2), using the bulk value (130 GPa<sup>16</sup>) for copper modulus. This is an important assumption in our calculation that could be avoided if x-ray diffraction measurements using  $\sin^2\psi$  method would be possible in copper sublayers. However, the mechanical contribution of copper is very small compared to the substrate one: in Eq. (1), the  $E_{Cu}e_{Cu}$  term represents only 2% of the  $E_s e_s$  term. Consequently, possible effects of nonisotropic textured copper, if they exist, may only have little influence on the results concerning tungsten. The obtained values for tungsten constants are reported in Table III. These results clearly demonstrate that the elastic constants are sensitive to the microstructure: in the "3.1 nm" multilayer, the Poisson's ratio (0.359) is larger than the bulk one (0.284) while it is smaller in the "24.0 nm" multilayer (0.221); concerning the Young's modulus, a noticeable softening is evidenced in the case of the small period multilayer ( $E = 338$  GPa) while in the other one, tungsten modulus ( $E = 392$  GPa) is equal to the bulk value (400 GPa) within the uncertainties. It should be kept in mind that the values obtained via x-ray diffraction measurements describe the intragranular elastic behavior of tungsten layers.

Assuming tungsten layers are elastically isotropic (like bulk tungsten), the stiffness coefficients  $C_{ij}$  can simply be extracted from the measured  $E$  and  $\nu$ <sup>7</sup>. The calculated values are given in Table III. For the "24.0 nm" multilayer, we can note a softening of  $C_{11}$  and  $C_{12}$ ,  $C_{44}$  being equivalent to the bulk value. For the "3.1 nm" multilayer, an unambiguous softening of  $C_{44}$  is evidenced, which is consistent with the results generally reported in the literature<sup>3,4,5</sup>. On the contrary, the increase of  $C_{11}$  and  $C_{12}$  appears like a particular phenomenon that needs to be confirmed by further investigations. The bulk modulus  $B = 1/3 (C_{11} + 2C_{12})$  can also be calculated and values are reported in Table III. For the small-modulation-wavelength sample, the increase of  $C_{11}$  and  $C_{12}$  results in a  $B$  value 33% higher than the pure bulk tungsten one, which is rather surprising (Young's modulus is

15% smaller than the bulk tungsten one). Although the unit-cell defects (evidenced by the stress-free-lattice parameter variations) are very different when the modulation wavelength changes, this result is more probably due to interface effects in the growth direction that prevail over the extrapolated mechanical properties.

In addition to elastic strain measurements, a cracking phenomena was observed in the case of the “3.1 nm” multilayer when the measured intragranular elastic strain in tungsten was about 0.45 %. The corresponding values found in the literature for bulk tungsten elastic limit range from 0.4 to 0.9 %<sup>14</sup>, depending on the microstructure. *Ex situ* atomic force microscopy observations confirmed the presence of a network of straight cracks perpendicular to the tensile direction and regularly spaced (20 to 30  $\mu\text{m}$ ). This cracking phenomena reveals a weak cohesion between grains in this structure, due to the growth mode. Like the softening of tungsten intragranular shear coefficient ( $C_{44}$ ), this effect contributes to the reduction of the mechanical performances of this multilayer.

In conclusion, intragranular elastic properties of nanocrystalline tungsten thin films have been studied using an x-ray diffraction method combined with tensile testing. Microstructure and size effects on tungsten in-grain elastic constants have been evidenced in the case of W/Cu multilayers deposited by ion beam sputtering on Kapton<sup>®</sup> substrates with two values of the modulation wavelength. The variations of elastic constants can be correlated with the microstructure, in particular the stress-free lattice parameter. All these results concerning the various elastic constants and their combinations undoubtedly indicate basic differences in the microstructures of the small- and large-period multilayers. Further investigations will aim to find out interpretations of these experimental results in terms of interatomic potentials and cohesion energies.

## References

- <sup>1</sup>J.L. Bassani, V. Vitek, and I. Alber, *Acta metal. Mater.* **40**, S307 (1992)
- <sup>2</sup>J. Schiøtz, T. Vegge, F. D. Di Tolla, and K. W. Jacobsen, *Phys. Rev. B* **60**, 11971 (1999)
- <sup>3</sup>R. Danner, R.P. Huebener, C.S.L. Chun, M. Grimsditch, and I.K. Schuller, *Phys. Rev. B* **33**, 3696 (1986)
- <sup>4</sup>A. Fartash, E.E. Fullerton, I.K. Schuller, S.E. Bobbin, J.W. Wagner, R.C. Cammarata, S. Kumar, and M. Grimsditch, *Phys. Rev. B* **44**, 13760 (1991)
- <sup>5</sup>J. Pacaud, F. Martin, A. Michel, C. Jaouen, P. Djemia, and F. Ganot, *Mat. Res. Soc. Symp. Proc.* **615** (2001)
- <sup>6</sup>P.-O. Renault, K.F. Badawi, L. Bimbault, and Ph. Goudeau, E. Elkaïm, and J.P. Lauriat, *Appl. Phys. Lett.*, **73**, 1952 (1998)
- <sup>7</sup>K.F. Badawi, P. Villain, Ph. Goudeau, and P.-O. Renault, *Appl. Phys. Lett.* **80**, 4705 (2002)
- <sup>8</sup>Ph. Goudeau, K.F. Badawi, A. Naudon, G. Gladyszewski, *Appl. Phys. Lett.* **62**, 246 (1993)
- <sup>9</sup>M. Jaouen, J. Pacaud, C. Jaouen, *Phys. Rev. B* **64**, 144106 (2001)
- <sup>10</sup>C. Noyan, and J. B. Cohen, *Residual Stress Measurement by diffraction and Interpretation* (Springer, New York, 1987)



<sup>11</sup>V. Hauk, *Structural and residual stress analysis by non destructive methods: evaluation, application, assessment* (Elsevier, Amsterdam, 1997)

<sup>12</sup> Powder Diffraction Files n° 4-806 and n° 4-836 from the International Center for Diffraction Data (ICDD), USA

<sup>13</sup> J.A. Floro, E. Chason, R.C. Cammarata, and D.J. Srolovitz, *MRS Bulletin* **27**, 20 (January 2002)

<sup>14</sup> Ph. Goudeau, K.F. Badawi, A. Naudon, N. Durand, *Mat. Res. Soc. Symp. Proc.* **308**, 713 (1993)

<sup>15</sup> P.-O. Renault, K.F. Badawi, Ph. Goudeau and L. Bimbault, *Eur. Phys. J. AP* **10**, 91 (2000)

<sup>16</sup> G. Simmons, and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook* (M.I.T. Press, Cambridge, USA, 1971)

## Figure caption

Fig.1: Evolution of (a) the slope  $P_1$ , and (b) the intercept  $m_1$ , of the  $\sin^2\psi$  curves relative to tungsten as a function of the mean applied stress ( $F/S_{\text{total}}$ ), for the two values of the multilayer modulation wavelength  $\Lambda$ .

TABLE I: Main geometric and microstructural parameters of the two studied multilayers. An estimate of the x-ray stress  $\sigma_{\text{XRD}}$  and stress-free lattice parameter  $a_0$  in W sublayers is done using W bulk elastic constants (see Table III). The lattice parameter of bulk W is equal to 0.3165 nm<sup>12</sup>.

|   |                |                |
|---|----------------|----------------|
| <b>Modulation wavelength <math>\Lambda</math> (nm)</b>    | $3.1 \pm 0.1$  | $24.0 \pm 0.1$ |
| <b>Number of bilayers</b>                                 | 70             | 10             |
| <b>Atomic composition (%) (EDXS)</b>                      | 44% Cu/56% W   | 52% Cu/48% W   |
| <b>W layer thickness <math>e_{\text{W}}</math> (nm)</b>   | $2.0 \pm 0.1$  | $13.3 \pm 0.1$ |
| <b>Cu layer thickness <math>e_{\text{Cu}}</math> (nm)</b> | $1.1 \pm 0.1$  | $10.7 \pm 0.1$ |
| <b><math>\sigma_{\text{curvature}}</math> (GPa)</b>       | $-0.3 \pm 0.1$ | $-1.7 \pm 0.1$ |
| <b><math>\sigma_{\text{XRD}}</math> (GPa) in W</b>        | $-1.7 \pm 0.3$ | $-5.1 \pm 0.1$ |
| <b><math>a_0</math> (nm) in W</b>                         | 0.314          | 0.318          |

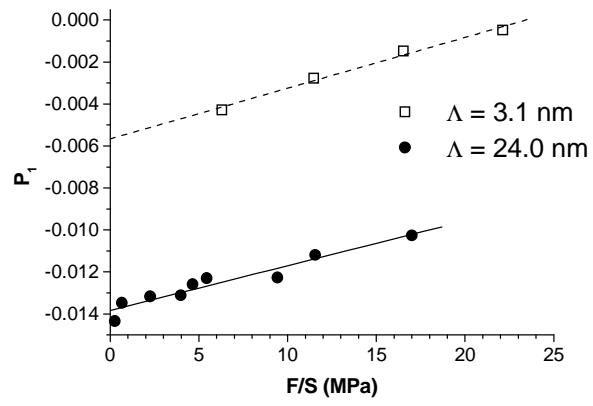
TABLE II: Examples of values of the total force applied to the specimen, with the corresponding intragranular elastic strains in tungsten layers deduced from x-ray diffraction measurements, for two values of the multilayer modulation wavelength  $\Lambda$ .

| <b><math>\Lambda = 3.1 \text{ nm}</math></b>  |         |         |         |         |         |
|---|---------|---------|---------|---------|---------|
| <b>Force (N)</b>                              | 0.35    | 2.25    | 4.1     | 5.9     | 7.9     |
| <b><math>\epsilon_{11}^A</math> (XRD)</b>     | 0.000 % | 0.152 % | 0.261 % | 0.360 % | 0.431 % |
| <b><math>\Lambda = 24.0 \text{ nm}</math></b> |         |         |         |         |         |
| <b>Force (N)</b>                              | 0.1     | 2.05    | 3.55    | 4.35    | 6.4     |
| <b><math>\epsilon_{11}^A</math> (XRD)</b>     | 0.000 % | 0.148 % | 0.165 % | 0.198 % | 0.340 % |

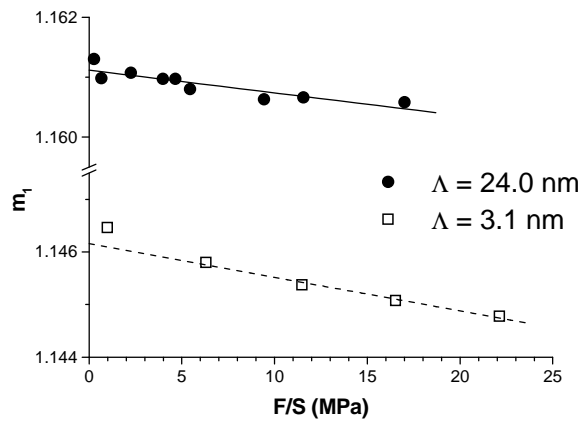
TABLE III: Values of the elastic constants ( $E$ ,  $\nu$ ) measured in the two W/Cu multilayers, and the  $C_{ij}$  constants and bulk modulus  $B$  deduced from these experimental values. Bulk tungsten reference values are given for comparison.

|  |                                 |                                  |                    |
|--|---------------------------------|----------------------------------|--------------------|
| <b>Modulation wavelength (nm)</b>        | <b><math>3.1 \pm 0.1</math></b> | <b><math>24.0 \pm 0.1</math></b> | <b><i>Bulk</i></b> |
| <b>Modulus <math>E</math> (GPa)</b>      | $338 \pm 65$                    | $392 \pm 60$                     | $400^a$            |
| <b>Poisson's ratio <math>\nu</math></b>  | $0.359 \pm 0.014$               | $0.221 \pm 0.003$                | $0.284^a$          |
| <b><math>C_{11}</math> (GPa)</b>         | 565                             | 448                              | $501^a$            |
| <b><math>C_{12}</math> (GPa)</b>         | 316                             | 127                              | $198^a$            |
| <b><math>C_{44}</math> (GPa)</b>         | 124                             | 160                              | $153^a$            |
| <b>Bulk modulus <math>B</math> (GPa)</b> | 400                             | 234                              | $300^a$            |

<sup>a</sup> See Ref. 16



(a)



(b)

Fig.1., P. Villain *et al.*, APL