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► **To cite this version:**

Raya El Beainou, Jean-Marc Cote, Valérie Potin, Nicolas Martin. Contrasted morphologies in nanostructured Janus W-Cu columns. *Materials Today Communications*, 2021, 27, pp.102331 (9). 10.1016/j.mtcomm.2021.102331 . hal-03360021

**HAL Id: hal-03360021**

**<https://hal.science/hal-03360021>**

Submitted on 24 Apr 2023

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## Contrasted morphologies in nanostructured Janus W-Cu columns

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### Abstract

Janus-like W-Cu films exhibiting a tilted columnar architecture are prepared by GLAD co-sputtering using W and Cu targets. Co-deposition of these two-immiscible metals leads to contrasted morphologies in the columns growth. Observations by scanning electron microscopy reveal different structural features at the micro- and nanoscales as the tilted columns face W or Cu target. In front of the W flux, columns are dense with a saw-tooth profile, whereas a granular and rough aspect is produced for the opposite side receiving Cu atoms. A finer structural analysis by high resolution transmission electron microscopy supports these different morphologies. Growth mechanisms as well as occurrence of diverse crystallographic phases (bcc  $\alpha$ -W, fcc Cu and even a disordered  $W_xCu_{1-x}$  alloy despite immiscibility of W and Cu metals) through the cross-section of the columns are discussed.

### Keywords

Janus tilted columns, GLAD, co-sputtering, electron microscopy.

### 1. Introduction

By analogy with the two-faced Roman God, Janus particles were suggested by de Gennes when he made his Nobel Laureate speech in 1991 [1]. Various Janus systems (especially nanoparticles) were successfully synthesized and characterized leading to exciting properties. Such systems have attracted attention these last years and showed potential in many applications [2]. However, differences in the material properties render the fabrication of Janus systems difficult. It is a challenge to prepare films exhibiting a Janus-like columnar structure by vacuum processes such as sputtering. Recently, GLancing Angle Deposition (GLAD) co-sputtering involving two sources was implemented to get metallic films [3] exhibiting a columnar architecture with a more or less defined Janus design. These few studies showed that nature of sputtered metals is not the

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only criterion for getting a well-separated two components system. Growing conditions are also relevant factors affecting quality of the Janus architecture.

In this letter, we report on some contrasted morphologies in tilted columnar W-Cu films prepared by GLAD co-sputtering. These two metals are chosen due to their immiscibility to favor a two-component feature inside a column. In addition, the growth of Janus-like columns particularly represent a scientific motivation for understanding growth mechanisms during the GLAD co-sputtering processes. A 4-view imaging of the slanted columns demonstrate their elliptical cross-section with a dense morphology for the columns side facing the W target, whereas a granular aspect of the copper grains is produced for the side exposed to the Cu flux. A finer analysis proves that Janus-like columns are grown with various orientations of W and Cu phases through the columns section.

## 2. Material and methods

W-Cu films were prepared by DC magnetron co-sputtering. A 40 L vacuum chamber was pumped down to  $10^{-5}$  Pa. W and Cu targets were used (99.9 at. % purity and 51 mm diameter). W target current was kept at  $I_W = 140$  mA and that of Cu at  $I_{Cu} = 40$  mA. The argon pressure was fixed at 0.40 Pa. Substrates were (100) Si wafers and located at the center of the substrate holder. The latter was inclined at an angle  $\alpha$  of  $80^\circ$  towards the normal of W and Cu targets (i.e.,  $\alpha_W = \alpha_{Cu} = 80^\circ$ ). The W target-to-substrate centers distance  $d_{W-S} = 65$  mm, and that of Cu  $d_{Cu-S} = 95$  mm. The deposition time was adjusted to get a 1  $\mu\text{m}$  thick film. Morphology of W-Cu films (surface and cross-section) was observed by scanning electron microscopy (SEM) in a dual beam SEM/FIB FEI Helios 600i microscope. Cross-sectional samples were prepared by focused ion beam (FIB) and Ga<sup>+</sup>-ion milled to electron transparency. The fine structural analysis was performed with a JEOL JEM 2100 FEG Transmission Electron Microscope (TEM) operating at 200 keV. TEM images were analyzed using the GATAN Digital Micrograph software and simulated with the Java Electron Microscopy Software (JEMS). The chemical composition was determined by energy-dispersive X-ray spectroscopy (EDX) in STEM (Scanning Transmission Electron Microscopy) mode by means of a BRUKER Quantax XFlash 5030T SDD.

## 3. Results and discussion

Top and cross-section SEM views of W-Cu thin films reveal some microstructural differences (Fig. 1). This morphological disparity has ever been reported by El Beainou *et al.* for GLAD W films [4]. It becomes more significant for GLAD co-sputtered W-Cu films. The surface view shows elongated cross-sections perpendicular to W and Cu fluxes (Fig. 1a). This

asymmetry is typically observed in GLAD films involving metals with a low self-diffusion length like W. Since our operating conditions favor the W flux ( $I_W = 140$  mA and  $I_{Cu} = 40$  mA, a shorter target-to-substrate distance for W than Cu), the W growth predominates and rules the orientation of the columns shape. This is illustrated from the cross-section observation. Columns are tilted in the direction of the W flux with a column angle  $\beta = 47^\circ$  (Fig. 1b). It is worth noting that both views (top and cross-section) show a smooth profile of the column side facing W flux, whereas a granular aspect is observed on the opposite side (facing Cu flux). These different features are evidenced by the two other views imaging columns in front of Cu (Fig. 1c) and W fluxes (Fig. 1d). A compact and flat aspect is produced on the column side receiving W atoms. The short W target-to-substrate distance, the high mass of W atom and their low mobility favor the growth of a dense microstructure. A rough and irregular appearance is rather noticed on the columns siding the Cu flux (Fig. 1c). A ragged profile is observed with grains, which are spread on the columns side receiving Cu atoms. This contrasted morphology between the opposite sides of the tilted columns is also connected to a high thermally induced mobility of Cu compared to W atoms, and the immiscible W-Cu system. As previously reported for the deposition of W and Au GLAD films [5], the columns growth mechanism is connected to arrival rates and energy of W and Cu atoms impinging on the columns. Their final morphology particularly depends on self-diffusion length of atoms and thus to the surface self-diffusion activation energy  $E_d$  ( $E_d$  is one order of magnitude higher for atoms like W, Mo or Ta than that of Au, Cu or Ag atoms [6]). As a result, the self-diffusion length of Cu is higher than that of W leading to a granular shape of the columns side facing Cu target and a dense morphology on the opposite side. Columns are W-rich and a single column grows with an elongated cross-section shape (perpendicular to W and Cu fluxes) composed of 2 components, i.e., a dense and majority part of W covered by grains of Cu.

This Janus-like structure is again illustrated from cross-section observations by TEM after the FIB preparation (X-ray diffraction analysis previously performed [7] did not supply a clear understanding about the phase occurrence and distribution in these W-Cu columnar films). In dark-field STEM images (Fig. 2a, 2c), brighter columns correspond to W, whereas darker parts to Cu. Up to 100 nm thickness, a dense thin lateral structure composed of W and Cu is produced at the film/substrate interface (Fig. 2a). A further increase of thickness leads to larger columns and voids appear between columns. For the biggest columns, W and Cu are clearly observed. A higher magnification evidences this 2 components feature (W dark and Cu bright in TEM mode) in a column (Fig. 2b). A granular morphology with defects is observed on the Cu side of the columns (brighter), whereas a dense W part (darker) is distinguishable close to the W/Cu interface with a fishbone-like shape on the opposite side. W and Cu are also viewed with a frank interface following the column axis (opposite contrast in

TEM images, Fig. 2c). To finely characterize these singular morphologies, two zones of the column cross-section (sides facing W and Cu targets; white rectangles in Fig. 2b) have been magnified (Figs. 3a, 3b). The saw-tooth-shaped aspect of the W part of the columns corresponds to the growth of the  $\alpha$ -W phase following the [110] direction. It is connected to the [100] preferential growth direction typical of bcc crystals [8]. Such a preferential growth is due to the high solidification velocity during condensation of W atoms on columns. HRTEM images acquired in the saw-tooth part (Fig. 3a), combined with FFT analyses highlights the occurrence of the  $\alpha$ -W phase. Experimental and simulated images (FFT from JEMS in Fig. 3) support the presence of crystallographic planes perpendicular to the growth direction of the column (facing W target), corresponding to  $d_{110} = 0.224$  nm of the bcc  $\alpha$ -W phase with a [001] zone axis. On the opposite side, nanometric grains are observed with {111} planes of the fcc Cu phase. The [101] zone axis is viewed corresponding to Cu nanoparticles from HRTEM and confirmed by JEMS with  $d_{111} = 0.211$  nm (Fig. 3b). Moreover, STEM-EDX analyses show W (blue) and Cu (red) alternations from mapping and linescan (Fig. 2c-2g) confirming the occurrence of a Janus-like structure.

The W/Cu interface also shows bcc  $\alpha$ -W and fcc Cu phases. Interplanar distances  $d_{200} = 0.156$  nm and  $d_{110} = 0.224$  nm are measured, which are related to W and Cu, respectively. However, we cannot completely exclude the formation of the  $\beta$ -W metastable phase (A15 cubic structure). The latter is favored during the growth of W exhibiting a high concentration of structural defects [9], which are significant close to the W/Cu interface (Cu atoms disturb the growth of W). We can assume that the  $\beta$ -W phase is certainly present in the W part of the columns since structural defects systematically occur during the GLAD growth. In-between bcc  $\alpha$ -W and fcc Cu phases, magnification does not show a frank boundary and one may suggest the formation of  $W_xCu_{1-x}$  alloys despite the W and Cu immiscibility. Chemical composition profiles show that W and Cu concentrations inversely change. They reach 50 at. % in this W/Cu interfacial zone (Fig. 2g). Radic *et al.* reported that  $W_{50}Cu_{50}$  metastable and amorphous solid solution alloy can be achieved by the co-sputtering technique [10]. This compound well corresponds to our measured composition through the cross-section in a given column at the W/Cu interface. As a result, we can claim that our Janus-like W-Cu tilted columns exhibit a cross-section profile perpendicular to W and Cu fluxes, composed of the stacking structure as follows: bcc  $\alpha$ -W (+ A15  $\beta$ -W) / (disordered  $W_{50}Cu_{50}$  alloy) / fcc Cu.

#### 4. Conclusion

W-Cu thin films were prepared by GLAD co-sputtering. A tilted columnar microstructure oriented in the direction of the W flux was obtained with a Janus-like architecture. Different morphologies were observed between the two opposite sides of the columns. A dense and fishbone feature was grown on the column side receiving W atoms assigned to their high mass and

low mobility. A rough and granular shape was obtained on the opposite side facing Cu, which was attributed to a high thermally induced mobility of Cu atoms impinging on the W columns. Cross-sections of the columns exhibited a Janus-like structure following the columns axis. Different metallic phases were recorded, i.e., bcc  $\alpha$ -W phase, fcc Cu phase and the possible occurrence of the metastable  $W_{50}Cu_{50}$  solid solution alloy. This GLAD co-sputtering process led to a significant amount of defects especially close to the W/Cu interface, and thus the occurrence of the  $\beta$ -W phase cannot be completely excluded in the W part of the columns.

### **CRedit authorship contribution statement**

**Raya El Beainou:** Data curation. **Jean-Marc Cote:** Data curation. **Valérie Potin:** Writing. **Nicolas Martin:** Writing.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### **Acknowledgements**

This work was supported by the EIPHI Graduate School (contract ANR-17-EURE-0002), the Region of Bourgogne Franche-Comté and the French RENATECH network.

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### Figures caption

#### Figure 1

SEM observations of a) top, b) cross-section, c) facing Cu and d) facing W of W-Cu film. Arrows and symbols indicate W (blue) and Cu (red) fluxes.

#### Figure 2

Cross-section observations after FIB preparation of W-Cu film: a, c) in STEM mode, and b) by HRTEM. Chemical composition profiles g) by EDX through the column cross-section shown in c): d-f) alternations of W (blue) and Cu (red).

#### Figure 3

HRTEM of two selected-areas (white rectangles in Fig. 2b) and related simulated diffraction patterns. a) bcc  $\alpha$ -W phase on one side of the columns (facing W target) and b) fcc Cu phase on the opposite side (facing Cu target). [001] and [101] zone axes are obtained for W and Cu, respectively.

Figure 1

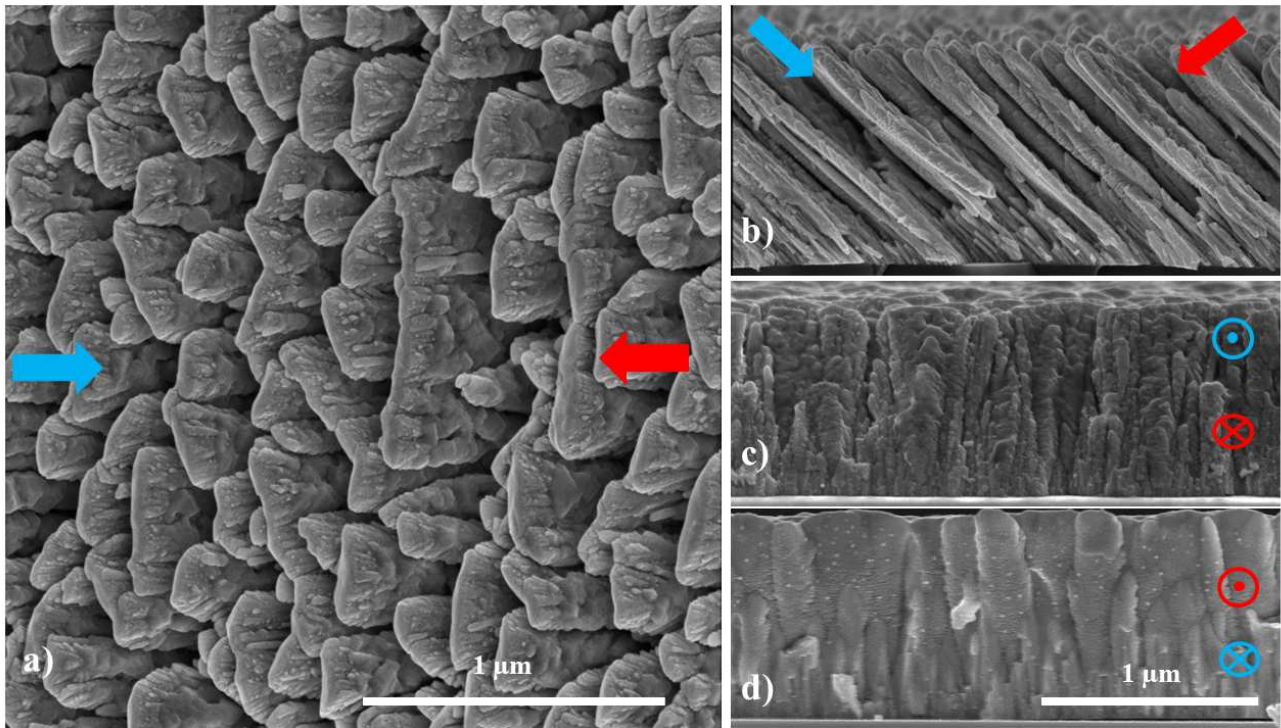




Figure 2

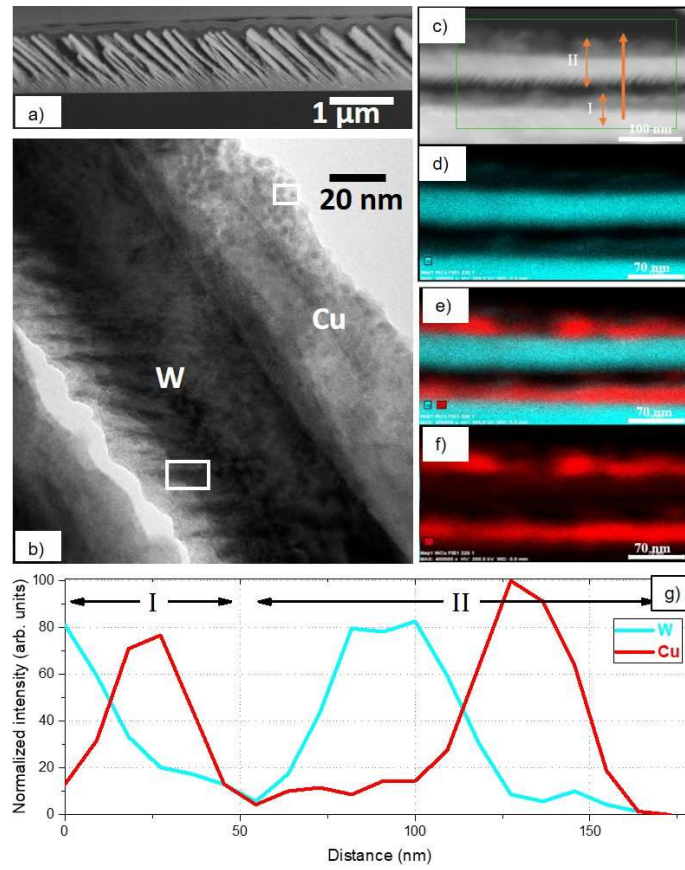
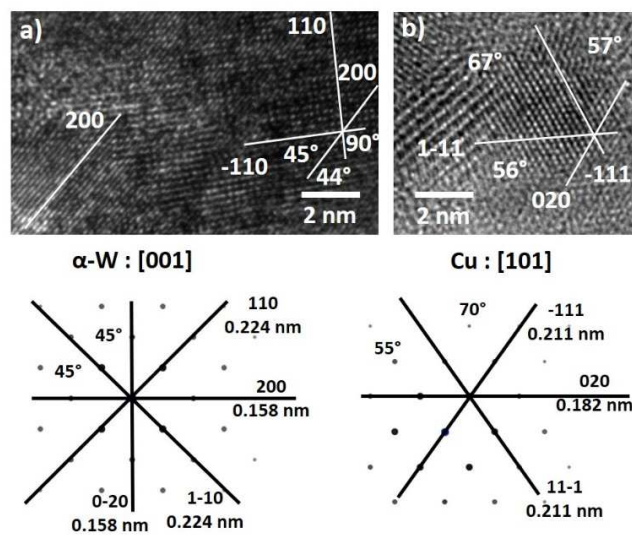


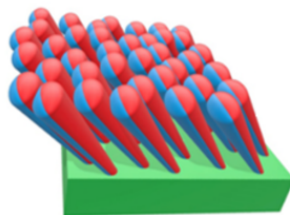
Figure 3



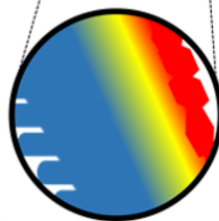
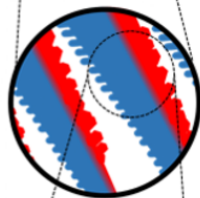
W flux



Cu flux



Janus-like architecture



$\alpha$ -W |  $\alpha+\beta$ -W |  $W_{50}Cu_{50}$  | fcc Cu