Supplementary material of

Chemical and electronic structure of buried W/Cu, W/Cr and W/Mo interfaces by in-situ XPS/HAXPES Auger parameter analysis

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S1. Surveys of the W/Cu, Cu/Mo and W/Cr multilayers, composites and the W metal, as measured by XPS and HAXPES

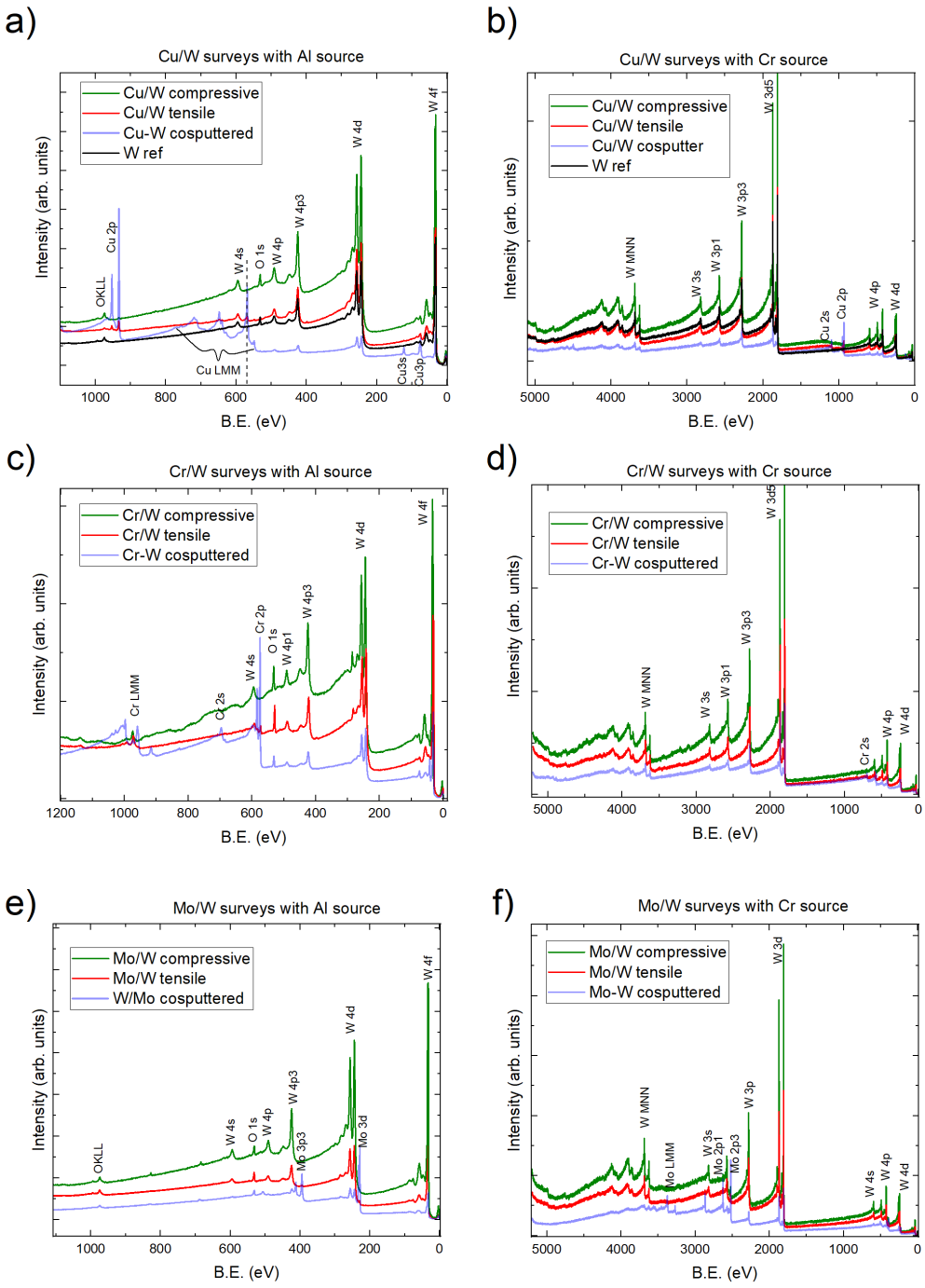

Fig. S1: Survey spectra of all the systems studies, as measured by soft Al and hard Cr X-ray sources. Survey spectra of all the Cu/W samples acquired with (**a**) the Al source and (**b**) the Cr source. Survey spectra of all the Cr/W system samples acquired with (**c**) the Al source and (**d**) the Cr source. Survey spectra of all the Mo/W system samples acquired with (**e**) the Al source and (**f**) the Cr source.

S2. Core levels and Auger transition analysis

All the samples presented in this study have been produced and XPS/HAXPES analyzed in-situ: direct transfer in UHV from the sputter chamber to the HAXPES chamber has been performed. In this way, the level of O and C on the surface were kept at the minimum. In order to be sure to collect enough signal from the interface, we always checked the detection of the buried layer (Cu, Mo or Cr) with the Al source. When the signal of the buried metal layer was too low and not measurable (in particular for compressive stress multilayers) by XPS, we reduced the thickness of the last W layer in the multilayer to~5-6 nm. For the tensile multilayers, due to the open structure with voids of the layers, there was no need to reduce the last W layer thickness as the buried layer signal was always clearly visible in all the studied systems. A detection of either Cu, Cr or Mo atoms from below the interface of the W top layer of each multilayer stack was verified by measuring the Cu 2p, Cr 2p or Mo 3d signal intensities (at a similar or lower KE values with respect to the W 4d and W $M_5N_7N_7$ peaks, corresponding to similar or smaller probing depths: see Fig. S2). For the tensile multilayers, the signal coming from Cu, Mo or Cr layers below the corresponding interface with the W top layer was always very clear due to the open grain boundary structure of the W tensile layers (see below and Ref. [1]). Here below are reported the core level comparisons between tensile and compressive multilayers of Cu/W, Mo/W and Cr/W.

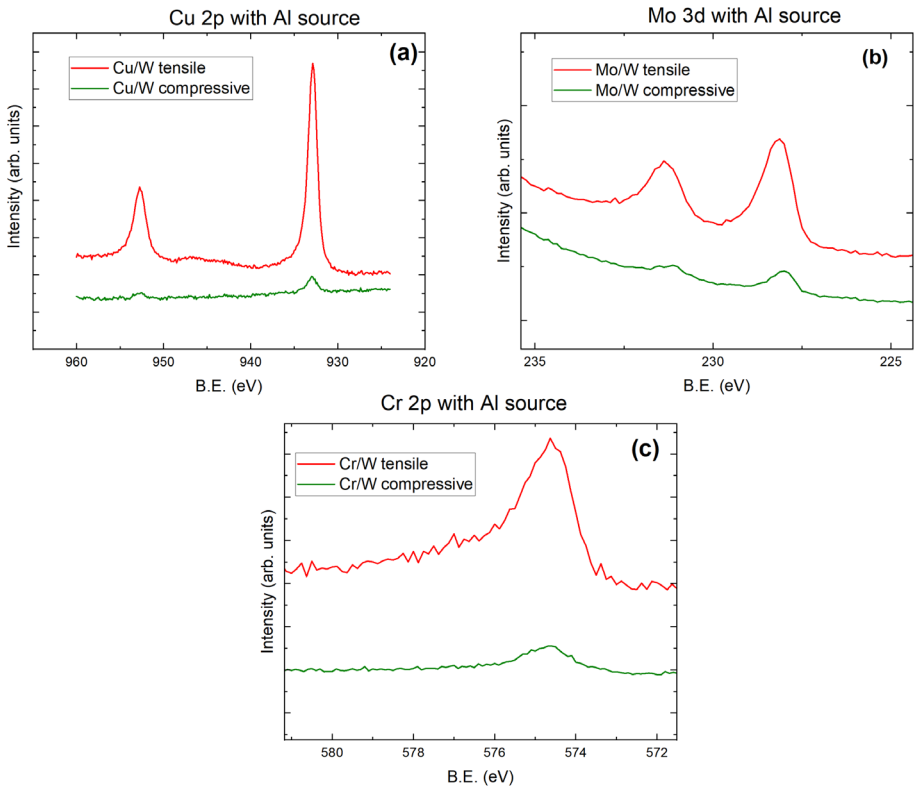

Fig. S2 (**a**) Cu 2p core levels acquired with Al source on a compressive and tensile multilayers. (**b**) Mo 3d signal acquired on compressive and tensile Mo/W multilayer. **(c)** Cr 2p signal on compressive and tensile Cr/W multilayers.

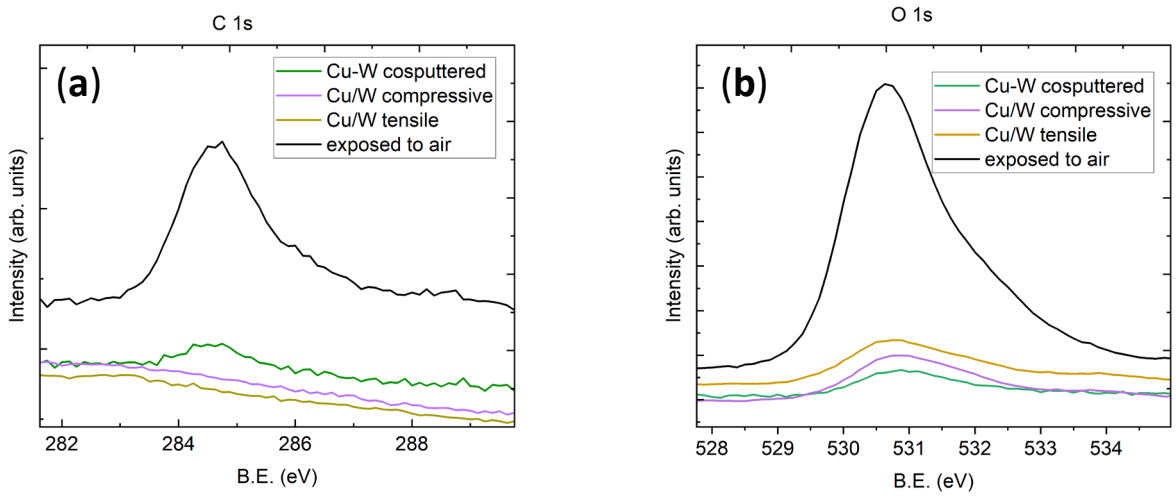

Fig. S3: (**a**) C1s and (**b**) O 1s core levels collected for the in-situ transferred Cu/W samples and the Cu/W compressive exposed to air.

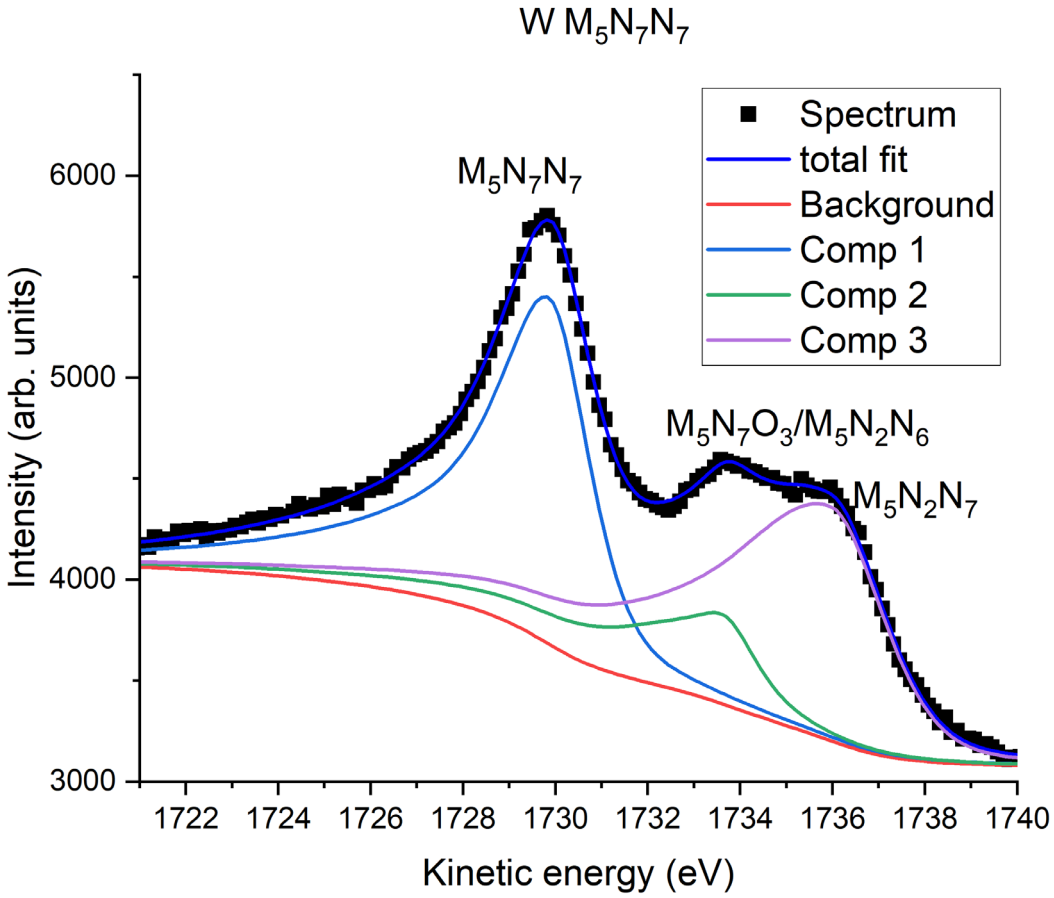

Fig. S4: Measured W MNN – MNO Auger transition region of pure W metal (as measured with the Cr X-ray source). The continuous curves represent the fit performed using 3 asymmetric Gaussian-Lorentzian functions and a Shirley background. The most intense Auger transition around 1730 eV

(in blue) is assign to the $M_5N_7N_7$ transition, as used for the Auger parameter study in the present work. The intermediate and weakest fitted peak components around 1736 (violet, intermediate intensity) and 1734 eV (green, weakest component) are both assigned to the $M_5N_7O_3$ / $M_5N_2N_6$ / $M_5N_2N_7$ Auger transitions.[2, 3] The same fitting conditions were used to fit the W MNN in all the samples studied. In fig. S3, the C 1s and O 1s core levels are shown in comparison to an air-exposed sample. In Fig. S4, an example of the W MNN Auger transition from pure W reference as fitted with 3 components is shown. The same fitting conditions, i.e. FWHM and distances between the peaks, have been applied for the other samples.

S3. Structural Analysis by XRD

The XRD diffractograms of all the systems studied are reported in Fig. S5. For Cu-W and Cr-W, clear peak separation between W and –Cu, Cr reflections is observed. The cosputtered samples for these 2 systems also show peak asymmetry indicating the presence of phase separated nano-grains of pure W and pure Cu or Cr. The Mo-W system instead, evidences clearly the formation of a solid solution for the cosputtered multilayer and extended intermixed layer at the interface for the sequential multilayers, as we reported in Ref. [4].

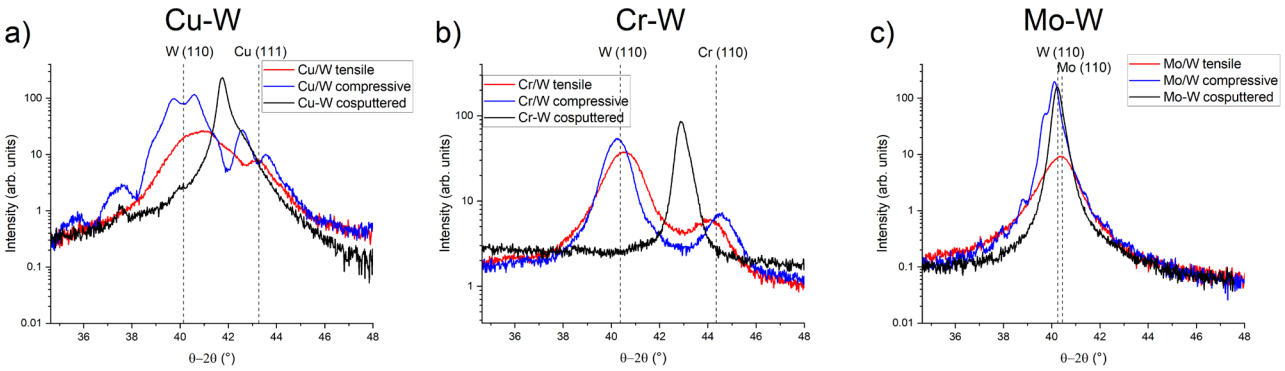

Fig. S5: X-ray diffractograms of a) Cu-W, b) Cr-W and c) Mo-W systems. The dashed lines indicate the theoretical position of bulk W (110), Cr(110), and Cu(111). The Cu, Cr and W peaks are clearly distinguished in all the systems except for Mo-W (Fig. S5 c). In the immiscible Cu/W multilayers typical superlattice oscillations, i.e. satellite peaks are observed and extensively analysed in Refs. [1, 5]. The analysis of superlattice fringes indicate phase separation between the layers of Cu and W.

S4. Sheet Resistance

As discussed in Sec. 3.2 in the main text, a positive AP shift of W in contact with Mo (and Cr) indicates an enhanced electronic screening with respect to the pure W metal. To prove this, sheet resistance for all the systems has been measured. The results are reported in Fig. S6. In line with the photoemission results, the resistance of the interfaces studied between W and either Cu, Mo or Mo is smallest when W is in contact with Mo, thus demonstrating a more "metallic-like" environment, as associated with enhanced electronic screening and thus a positive AP shift with respect to pure W metal. However, interfacial scattering also contributes to resistance in multilayers. Sharper interfaces, such as those in Cu/W, exhibit higher scattering and thus higher resistance.

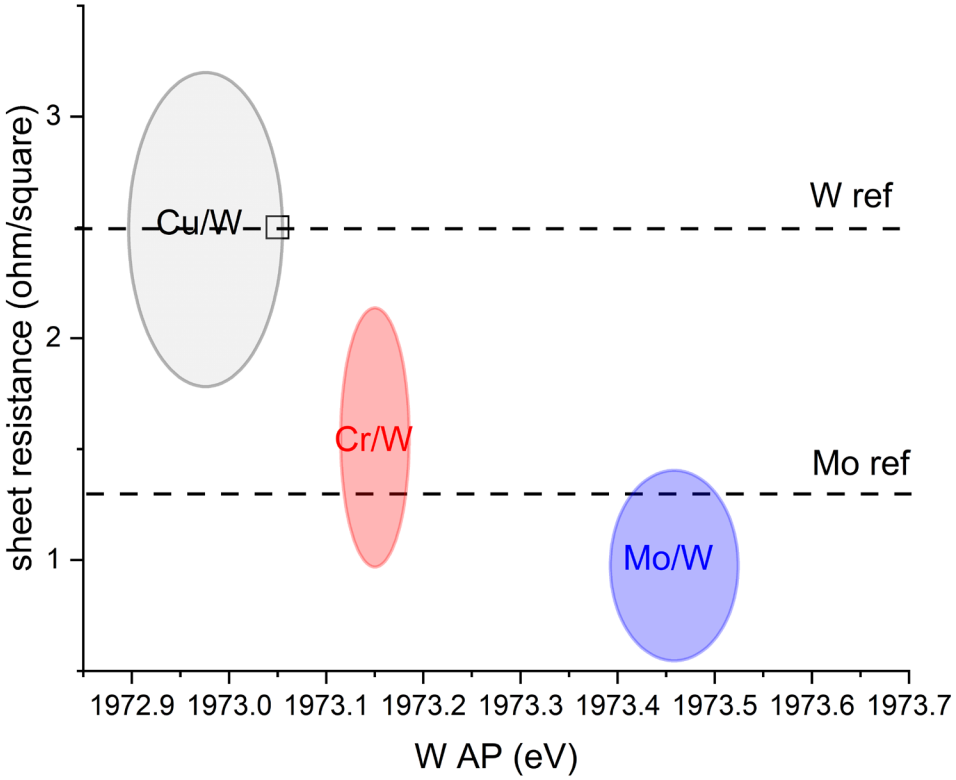

Fig. S6 Resistance measurements of the three W-based binary alloy systems investigated, plotted as a function of the measured AP of W. The three shaded regions indicate the range of values measured, including uncertainty for each system studied. The dashed lines indicates the sheet resistance measured for pure sputter grown W and Mo layers, 200 nm thick. The square point represent the AP measured for the pure W reference sample.

S5. *Ab initio* calculations with B2 simulation cells for Cu/W, Mo/W and Cr/W

Given the absence of any accurate experimental and/or empirical methods to predict charge transfer at the interfaces studied, first-principles density functional theory (DFT) was applied to study the electronic charge distributions at the W/Cu, W/Cr and W/Mo interfaces. To this end, B2 simulation cells (bcc cell with two basis atoms occupied by two different elements) with a 50/50 at.% stoichiometry (i.e. *X*-W with 50 at.% for *X* = Cu, Mo, and Cr) were constructed, thus every nearest neighbor of a W atom is an atom *X* and vice versa. Notably, the B2 unit cell disregards any structural differences between the different interfaces due to the initial lattice mismatch (i.e. Mo/W interfaces have bcc crystal structures with similar lattice parameters, which generally results in coherent interfaces. Cu (fcc) and Cr (bcc) exhibit a much larger initial lattice mismatch with the bcc W unit cell, resulting in incoherent interfaces). The calculated change in Bader charge for W atoms in the simulated *X*-W B2 structures (with respect to a pure W bcc unit cell) are -0.37e, 0.05e, and 0.20e for *X* = Cu, Mo, and Cr, respectively: see Fig. S7. A positive change in Bader charge for W implies a predicted transfer of electron charge from the neighboring atoms *X* to W.

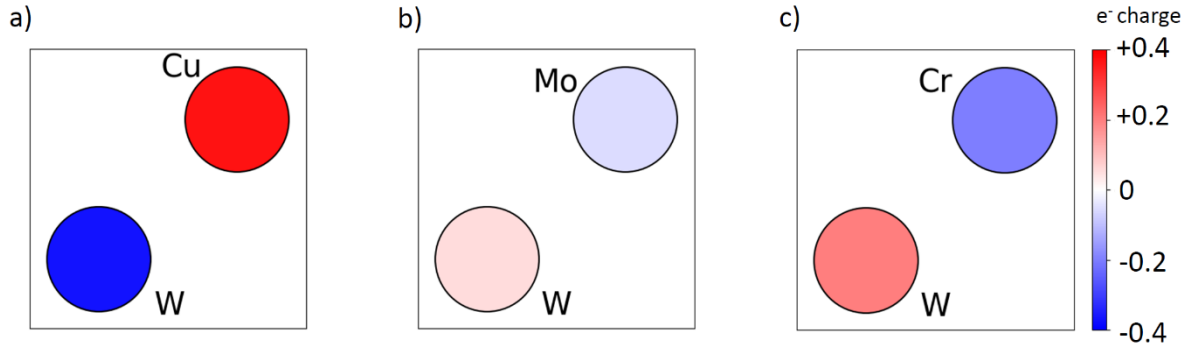

Fig. S7 Charge transfer from DFT simulations for the X-W B2 structures (X = Cu, Mo, and Cr; as compared to a pure W bcc unit cell). The charge transfers are given in unit of electron charge. W and X are distinguished by the orange and cyan outlines. A positive change in Bader charge for W implies a predicted transfer of electron charge from the neighboring atoms X to W.

The charge transfers of 0.05e from Mo to W and of 0.20e from Cr to W, respectively, are consistent with the expectations from the electronegativity of the elements. The relative difference between the electronegativity of Mo and W (Mo – 2.16 and W – 2.36) is lower than that of Cr and W (Cr – 1.66 and W – 2.36), in accord with the predicted smaller charge transfer from Mo to W. However, these model predictions do not correctly predict the trend in the W AP shift, since a larger shift is observed for Mo than for Cr (see Fig. 6).

References

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