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Supporting Information

# C 1s Peak of Adventitious Carbon Aligns to the Vacuum Level: Dire Consequences for Material's Bonding Assignment by Photoelectron Spectroscopy

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## Methods

The adventitious carbon layers analyzed in this study are accumulated on the surfaces of polycrystalline (TM)N thin films, where TM = Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, and W grown by reactive dc magnetron sputtering in $Ar/N_2$ gas mixtures. The total pressure $P_{tot}$ during all depositions is kept constant at 3 mTorr (0.4 Pa), while the $N_2$–to-Ar flow ratio is optimized for each target material to obtain stoichiometric single-phase nitrides. Si(001) is used as a substrate and the film growth is performed at the temperature $T_s$ of 470±12 °C. To minimize surface roughness, the resulting film thickness is kept relatively low, from 140 nm for TiN to 420 nm for WN. Following the growth, the vacuum vessel is evacuated with $N_2$ (99.999 % pure) once the sample temperature drops below 230 °C in order to ensure consistency of obtained results,[i] which typically requires ~100 min wait. Samples are subsequently exposed to laboratory air (40 % RH, 23 °C) for less than 2 min necessary to transfer them to the ultra-high-vacuum (UHV) XPS system. Further details about (TM)N layers including elemental composition, crystalline structure, and surface roughness can be found in reference [ii].

C 1s and valence band (VB) XPS spectra are recorded in Axis Ultra DLD instrument (Kratos Analytical, UK) employing monochromatic Al Kα radiation (hν = 1486.70 eV). The base pressure during spectra acquisition is $1.1\times10^{-9}$ Torr ($1.5\times10^{-7}$ Pa). The same instrument is used for work function $\phi_{SA}$ measurements performed using ultraviolet photoelectron spectroscopy (UPS) with unmonochromatized He I radiation (hν = 21.22 eV). $\phi_{SA}$ is obtained from the secondary electron cutoff energy in the He I UPS spectra, according to the standard procedure described in detail elsewhere,[iii] with the accuracy of ±0.05 eV. $\phi_{SA}$ of the sputter-cleaned reference Au sample is 5.30 eV, which agrees very well with the textbook values that span from 5.0 to 5.4 eV.[iii] The binding energy scale is calibrated by examining sputter-cleaned Au, Ag, and Cu samples according to the recommended ISO standards for monochromatic Al Kα sources that place Au $4f_{7/2}$, Ag $3d_{5/2}$, and Cu $2p_{3/2}$ peaks at 83.96, 368.21, and 932.62 eV,

respectively.[iv,v] The Fermi level cut-off for all three metal samples defines the "0" of the BE scale. The charge neutralizer was not used in any of the reported experiments. C 1s peak models are constructed using CasaXPS software,[vi] Shirley type background[vii] (except for the spectra recorded from MoN and WN samples, where linear background was necessary), and Voigt functions with 70% Gaussian contribution.

Samples are first analyzed in the "as-received" state, i.e., following the ~100 min long exposure to residual gases in the growth chamber and <2 min long ambient exposure. After that all TMN surfaces are sputter-etched with 0.5 keV $Ar^+$ ions incident at an angle of 70° with respect to the sample normal. The ion beam is rastered over a 3×3 $mm^2$ area, while the analysis area is 0.3×0.7 $mm^2$ and centered in the middle of the ion-etched crater. XPS and UPS characterization is then performed on cleaned surfaces and following the exposure to laboratory air for 10 min, 100 min, 1 day, 1 week, 1 month, and 7 months. The thickness of AdC layers are estimated from the relative intensities of core level signals using a Hill equation.[viii]

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[i] G. Greczynski, S. Mráz, L. Hultman, J.M. Schneider, *Appl. Phys. Lett.* **2016**, 108, 041603

[ii] G. Greczynski, D. Primetzhofer, J. Lu, and L. Hultman, *Appl. Surf. Sci.* **2017**, 396, 347

[iii] see for example: Chapter 1 in S. Hűfner "Photoelectron Spectroscopy: Principles and Applications", 3rd Ed. Springer **2003**, ISSN 1439-2674

[iv] M.P. Seah, *Surf. Interf. Anal.* **2001**, 31, 721

[v] ISO 15472, "Surface chemical analysis- *x*-ray photoelectron spectrometers - calibration of energy scales" (ISO, Geneva, **2001**)

[vi] See N. Fairley "XPS Lineshapes and Curve Fitting" in "Surface Analysis by Auger and X-ray Photoelectron Spectroscopy" Ed. D. Briggs and J.T. Grant, IM Publications, Manchester, **2003**, p.397

[vii] D. A. Shirley, *Physical Review B* **1972**, 5, 4709

[viii] we estimate the thickness $d$ of the adventitious carbon from the Hill equation: $d = \lambda ln(1 + (I_O/s_O)/(I_S/s_S))$, in which $I$ stands for signal intensity, $s$ is the sensitivity factor, and $\lambda$ is the mean free path for electrons with the energy of 1 keV in the carbon overlayer (here 20 Å, based on values given in Ref. **Fehler! Textmarke nicht definiert.**). Indices "O" and "S" refer to carbon overlayer and the substrate. See: P.J. Cumpson "Angle-resolved XPS" in "Surface Analysis by Auger and X-ray Photoelectron Spectroscopy", edited by D. Briggs and J.T. Grant, IM Publications and Surface Spectra Limited (UK), 2003.