Short Communication

Referencing to adventitious carbon in X-ray photoelectron spectroscopy: Can differential charging explain C 1s peak shifts?

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A B S T R A C T

C 1s peak of adventitious carbon (AdC), often used for charge referencing XPS spectra, shows markedly large shifts from the "recommended" value of 284.8 eV that basically disqualifies its reliability. In some earlier papers we attributed this spreading effect to the vacuum level (VL) alignment at the AdC/sample interface, which makes the measured position of C 1s peak E_B^F highly sensitive to the sample work function ϕ_{SA}. Recently, it was suggested [M.C. Biesinger, *Appl. Surf. Sci.* 597 (2022) 153681] that it is instead the differential charging in the native oxide layers that sometimes accounts for C 1s shifts and that electrically isolating samples from the spectrometer would solve the problem. To evaluate this hypothesis, we performed a series of experiments with Au and Al foils electrically isolated from the spectrometer, while varying the surface potential in a relatively wide range by adjusting the charge neutralizer settings. Markedly, the C 1s peak positions recorded from Au and Al foils are distinctly different when referred to their Fermi levels, at respectively 284.80 ± 0.05 eV and 286.31 ± 0.06 eV, independent of the surface potential. This confirms the interpretation presented in our previous papers (experiments performed in a conventional way with samples connected to spectrometer), that the binding energy of C 1s peaks from Au and Al foils differs significantly due to the corresponding difference in their work function values, such that the sum $E_B^F + \phi_{SA}$ is constant at ∼ 289.6 eV, as imposed by the VL alignment. In addition, the energy separation between metal and oxide peaks in Al 2p spectra from Al foil is independent of the surface potential (controlled by the charge neutralizer settings), the photoelectron current (varied by adjusting x-ray power) and the Al oxide thickness (in the range from 0.7 to 4.7 nm). These observations disprove differential charging as the general cause of C 1s peak shifts at least for the case of Al foils with thinner oxide layers. As many thicker oxides are well-known to develop charging, a similar type of analysis can be performed on the case-to-case bases to determine the reasons for C 1s peak shifts.

1. Introduction

The criticism against using the C 1s peak of adventitious carbon (AdC) for charge referencing of XPS spectra is as old as the method itself. [1–5] The history of doubts, questions, and warnings towards this method was reviewed recently. [6] The main concerns raised are the unknown and multiple chemical identity of AdC, its unknown origin, and the uncertainty related to the binding energy (BE) values assigned to the C 1s peak of a given AdC. Over the last years, we have published articles on different aspects of the subject based on extensive evidence from thin film samples deposited by magnetron sputtering.[7–9] These systematic studies established facts that in our opinion disqualify the C 1s peak of AdC from what could be considered a reliable charge reference. These are:

(1) The chemical form of AdC depends on the substrate, the type of environment it has been exposed to, and the exposure time,[6].
(2) The BE of the C-C/C-H C 1s peak of AdC depends on the substrate it accumulates on and may vary by as much as 2.66 eV for the range of materials systems tested by us, which covered transition metal (TM) nitride, carbide, boride, and oxide thin film samples [9]. Similar spread in the C 1s peak position was also reported by Crist, [10].
(3) referencing to the C 1s peak, as recommended by ISO/ASTM standards, [11,12] may lead to unphysical results, like a non-zero density of states above the Fermi level (FL), [7,8].
(4) C 1s shifts caused by the substrate are larger than typical chemical shifts, which prevents any meaningful bonding assignments, [9].

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(5) The sum of the C-C/C-H C 1s peak BE E_B^F and the sample work function ϕ_{SA}, is constant; for nearly one hundred analyzed samples, representing a wide range of material classes and for air exposure times varying from 10 min to 7 months, we determined that $E_B^F + \phi_{SA} = 289.58 \pm 0.14$ eV,[9].

(6) $E_B^F + \phi_{SA} = $ constant, indicates invariant binding energy of the C 1s peak with respect to the vacuum level (VL). This VL, rather than the commonly assumed FL alignment, results from the fact that AdC is not an inherent part of the analyzed sample and as such may not remain in proper electrical contact with the substrate (and spectrometer),[6,9].

(7) Since the BE of the C 1s peak is steered by the sample work function, it cannot serve as a reliable reference for calibrating the BE scale. [6,8,9].

The problem was further illustrated in an experiment by mounting Al and Au foils side by side, *in electric contact with each other and to the spectrometer*, and recording the C 1s spectra of AdC across the interface. [13] The C 1s C-C/C-H peak split into two if spectra were recorded from both samples simultaneously. We explained this effect by the VL alignment between AdC and the substrate, which makes C 1s peak positions dependent on the sample work function. As the work function of the Al foil is 1.5 eV lower than that of the Au foil, C 1s peaks corresponding to the same chemical state of C appear at two distinctly different values of BE. The sum of C 1s BE and ϕ_{SA} is, however, constant, at 289.5 eV, in agreement with our earlier study.[9]

The above experiments were performed in a conventional way, that is with samples in good electrical contact with the sample holder as was confirmed by the fact that the Fermi level cut-off appeared at 0 eV. The above interpretation of C 1s shifts was, however, challenged in the very recent paper by Biesinger. [14] That work presents related experiments with Al and Au foils but *with samples electrically isolated from the spectrometer* and with the use of a charge neutralizer. It has to be emphasized that this creates entirely different experimental conditions as compared to the conventional XPS analysis of conducting samples. Thus, contrary to what is implied in Ref. 14, this is not a duplication of our experiment reported in Ref. 13, but a different type of experiment. Nevertheless, it was observed in Ref. 14 that the BE of the C 1s peak of AdC is constant at 285.18 eV while moving the analysis area from the "mostly Al" to the "mostly Au" part of the sample. What is somewhat confusing is that in the same paragraph it is stated that the C 1s peak recorded from the"Al-only" part of the sample was at 285.8 eV, i.e., 0.6 eV away from the "constant" value. This observation was not discussed further.

Without actually reproducing our experiments, the author of Ref. 14 claims that our results [9,13] showing different C 1s peak positions on different substrates are affected by differential charging that develops in surface oxide layers and shifts peaks to higher BE. Markedly, this statement is not supported with any experimental evidence that would actually prove the existence of differential charging effects in thin film samples with native oxide layers.

To address the matter, we have duplicated the experiment from Ref. 14 with Al and Au foils isolated from the sample holder. The former sample contains a few nm thick native oxide layer, in which the claimed differential charging is supposed to occur. To get more comprehensive understanding, we vary the charge neutralizer settings to record spectra with the surface in the electrically neutral state, as well as over- and under-compensated. At any flood gun setting, the positions of C 1s peaks from the Al and Au foils turn out to be constant with respect to their FL's and so are the positions of metal and oxide peaks in Al 2p spectra. The previously reported splitting of 1.5 eV between C 1s peaks from Au and Al foils [13] is confirmed for all flood gun settings (surface under and over-compensated) *provided that the corresponding FL's are used as reference*. We further show that it is possible to obtain C 1s peaks at the same BE from both substrates for specific charge neutralizer setting, however, that result is valid *only without reference to the FL*. Moreover, we present

additional arguments that disqualify differential charging as the plausible explanation of peak shifts for the case of thin film samples with native oxide thickness in the same range as relevant electron inelastic mean free paths.

2. Experimental details

XPS analyses are performed in an Axis Ultra DLD instrument from Kratos Analytical (UK) with the base pressure during spectra acquisition better than 1.1×10^{-9} Torr (1.5×10^{-7} Pa), achieved by a combination of turbomolecular and ion pumps. Monochromatic Al Kα radiation (hν = 1486.6 eV) is used with the anode power set to 150 W (with the exception for experiments reported in Sec. 3.3.2, in which case the x-ray power was varied from 225 to 15 W). The spectrometer is calibrated using the sputter-etched Au, Ag, and Cu samples. Au $4f_{7/2}$, Ag $3d_{5/2}$, and Cu $2p_{3/2}$ peak positions are confirmed to be within $\pm$ 0.02 eV from 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. [15] All spectra are collected at normal emission angle. The analyzer pass energy is 20 eV, which yields the full width at half maximum of 0.55 eV for the Ag $3d_{5/2}$ peak. The area analyzed by XPS is 0.3×0.7 mm^2. Spectra deconvolution and quantification is performed using CasaXPS software package and sensitivity factors supplied by the instrument manufacturer. [16].

3. Results and discussion

3.1. Au and Al foil experiments with samples electrically isolated from the spectrometer

Inspired by experiments performed in Ref. 14 we placed Au and Al foils on the glass substrate to electrically isolate them from the sample holder. As the charge neutralizer settings that control the surface potential appear to be a natural experimental factor in such configuration, we intentionally varied the neutralizer filament current I_N to create conditions of surface under- and over-compensation, while monitoring peak shifts. The surface potential is assessed directly from Au $4f_{7/2}$ and Al 2p (metal) peak shifts with respect to standard values of 83.96 and 72.9 eV.[15,17] The accuracy of this procedure is confirmed by analyzing corresponding shifts of the FL cut-off. The shifts of core level peaks and those for corresponding FL's are the same within $\pm$ 0.05 eV.

Fig. 1(a) shows the BE of the C 1s peak from the AdC layer (the strongest component commonly assigned to the C-C/C-H bonding) plotted as a function of charge neutralizer current. Data are recorded at the positions corresponding to either the Al or the Au foil and at least 5 mm away from the place where both samples connect. Corresponding results for the position of the FL cut-off are shown in Fig. 1(b). Clearly, both C 1s and FL shifts vary in a wide range as a function of low-energy electron flux sent to the surface. Initially, at lower current settings the electron flux is not sufficient to compensate surface charging due to photoemission. This condition is characterized by the position of the FL cut-off higher than 0 eV. Markedly, the neutralizer filament current necessary to bring the FL to zero eV (i.e., to reach the neutral condition) is not the same for Al and Au samples. The values are 1.32 and 1.41 A, respectively. Higher electron flux necessary for reaching neutral surface in the case of the Au foil can be explained by significantly higher photoelectron current owing to very high relative sensitivity factors (RSFs) for Au core levels with respect to those of Al (e.g., the RSF for Au 4f is ca. 32 times higher than that of Al 2p). With increasing filament current the electron flux to the surface increases. For higher neutralizer current settings, the surface becomes overcompensated as indicated by FL lower than 0 eV. In the limit of the highest neutralizer current setting tested, the FL from both samples approach the common limit of ca. −3.6 eV, corresponding to the case where the samples are flooded with electrons to the extent that the surface potential is solely determined by the neutralizer settings.
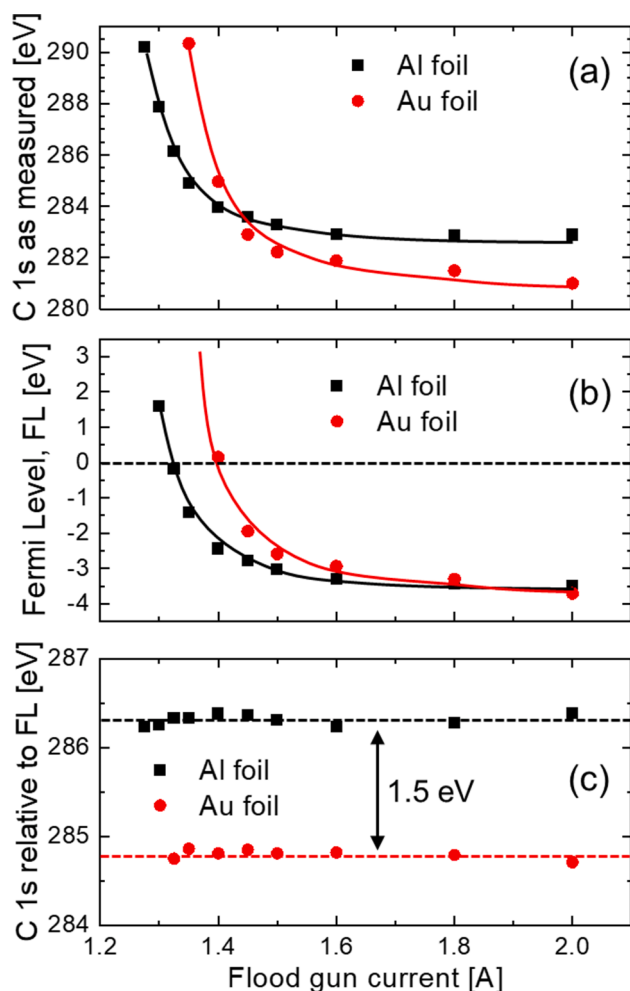
Fig. 1. (a) Binding energy (as recorded) of the C 1s peak from AdC layer (the strongest component commonly assigned to C-C/C-H bonding) plotted as a function of charge neutralizer current, (b) the corresponding Fermi level (FL) cut-off positions, and (c) the C 1s peak position plotted with respect to the FL. Spectra are collected from either an Al or an Au foil (both isolated from the spectrometer) and at least 5 mm away from the place where both samples connect.

The above changes in the surface potential are directly reflected in the measured C 1s shifts shown in Fig. 1(a). Two essential observations can be made here: (1) it is possible to find the neutralizer setting for which the apparent C 1s peak positions are the same for both samples (here this happens for $I_N = 1.42$ A), and (2) in the limit of the highest neutralizer current, the C 1s positions do not merge (as is the case for the FL's), but instead approach very different values with the C 1s from AdC/Au sample being at lower BE.

Reassuring for the case we are making, the C 1s peak position referenced to the sample FL is independent of charge neutralizer current (thus surface potential) for both samples. This result is illustrated in Fig. 1(c). The horizontal dashed lines mark the average values, which are 284.80 ± 0.05 eV and 286.31 ± 0.06 eV for the Au and Al foils. Thus, *the peak splitting of 1.5 eV reported in our previous paper* [13] *for the case of grounded samples is fully confirmed also for samples isolated from the spectrometer.* Noteworthy is the fact that the BE splitting is independent of the surface potential, which in the present experiment is varied from -3.7 to $+ 9.7$ V for the Au sample, and from -3.5 to $+ 4.0$ V for the Al foil.

Taking the above findings into account, one can demonstrate C 1s peak shift for samples electrically isolated from the spectrometer in either direction, when moving the analysis area from the Al to the Au

sample, by proper selection of charge neutralizer current. This result is illustrated in Fig. 2. In the first case (a) C 1s is recorded at $I_N = 1.35$ A (the Au foil surface is undercompensated under such conditions, while the Al foil surface is overcompensated). As a result, the peak position varies from 284.90 eV on the Al foil to 290.30 eV on the Au foil. Noteworthy, the C 1s peak does not jump directly to the latter value once the analysis area is moved over to the Au foil, but rather shows a gradual shift towards 290.3 eV. Such behavior can be an indication that the surface potential settles at the final value only as the entire electron flux produced by the charge neutralizer reaches the Au foil. The same experiment performed with a higher charge neutralizer current of 2.0 A (corresponding to the situation where both sample surfaces are over-compensated, cf. Fig. 2(b)) results in the C 1s shift in the opposite direction: from 282.90 eV on the Al foil to 281.0 eV on the Au foil. *Once again, we emphasize that the C 1s peak positions shown in Fig. 2 are as recorded values – if replotted with reference to the respective FL's only two distinct values are obtained: 284.80 for the Au foil and 286.31 eV for the Al foil* (cf. Fig. 1(c)). Noteworthy also is the fact that the C 1s peak position of 286.3 eV for the Al foil was independently confirmed in another laboratory [10].

Fig. 3 shows (a) the Al 2p and (b) Au $4f_{7/2}$ peak shifts recorded simultaneously with C 1s and FL spectra discussed above. Trends from varying the electron flux from the charge neutralizer are very similar: all peaks move towards lower BE values with increasing charge neutralizer current I_N. Importantly, once plotted with respect to FL values (cf. Fig. 1 (b)) all core level peaks exhibit BE that is independent of I_N: the Al 2p peaks are at 72.96 ± 0.03 and 76.07 ± 0.06 eV for metal and oxide contributions, respectively, while the Au $4f_{7/2}$ peak is at 84.08 $\pm$ 0.01 eV. The BE values for the Al 2p and Au $4f_{7/2}$ metal peaks agree very well with standards derived for Al_2O_3/Al without using the C 1s referencing, [18] and are in perfect agreement with those from samples in electrical contact with the spectrometer. Moreover, the spectral shape is preserved irrespective of surface potential as illustrated in Fig. 4 for the case of Al 2p spectra from the Al foil recorded for several values of the charge neutralizer current. The top panel (a) shows spectra as recorded for the case of a positively charged surface ($I_N = 1.275$ A, FL shift of 3.97 eV towards higher BE), a nearly neutral surface ($I_N = 1.325$ A, FL shift of 0.19 eV towards lower BE), or a negatively charged surface ($I_N = 2.0$ A, FL shift of 3.51 eV towards lower BE). The bottom panel (b) shows the same spectra referenced to their corresponding FL values. Markedly, all spectra are essentially identical. Hence, varying the surface potential
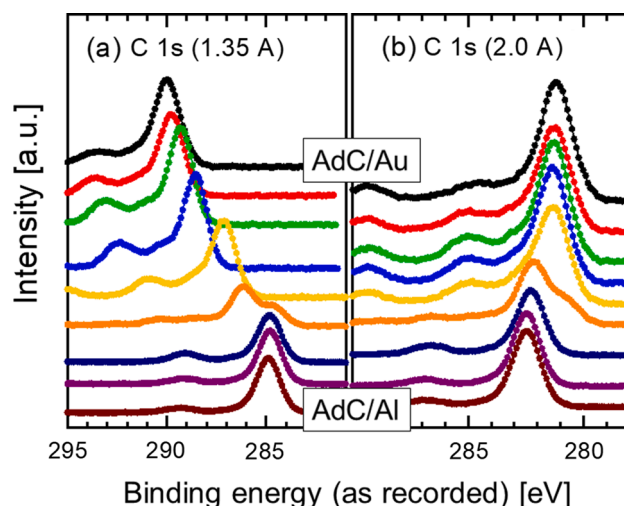

Fig. 2. C 1s of adventitious carbon recorded while moving the analysis area from the Al foil (at the bottom) onto the Au foil (on top) for the case of (a) charge neutralizer current $I_N = 1.35$ A (corresponding to an undercompensated Au surface and an overcompensated Al surface), and (b) $I_N = 2.0$ A (both Au and Al foils surfaces are overcompensated).
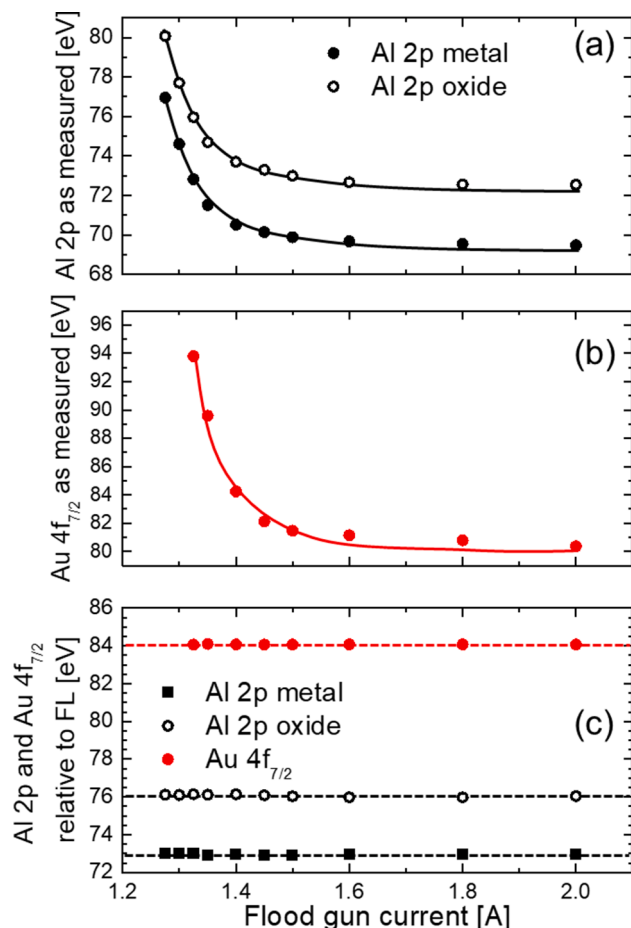
Fig. 3. (a) BE position (as recorded) of metal and oxide peaks in Al 2p spectra and (b) Au $4f_{7/2}$ peak position (as recorded) plotted as a function of charge neutralizer current. (c) peak positions from (a) and (b) replotted with respect to corresponding Fermi levels.

Fig. 4. (a) Al 2p spectra from the Al foil (isolated from the spectrometer) recorded for several values of charge neutralizer current: $I_N = 1.275$ A (a positively charged surface, FL shifts by 3.97 eV towards higher BE), $I_N = 1.325$ (a nearly neutral surface, FL shifts by 0.19 eV towards lower BE), and $I_N = 2.0$ A (a negatively charged surface, FL shifts by 3.51 eV towards lower BE). (b) Al 2p spectra from (a) referenced to their corresponding FL values.

from −3.97 V (green spectrum) to + 3.51 V (black spectrum) has no effect on the spectral shape. In particular, the metal – oxide peak splitting is identical in all three cases and the same to that obtained from samples in good contact to the spectrometer.

The above results are in apparent contradiction to what was reported in Ref. 14. In that paper it was shown that the C 1s peak from Al and Au foils isolated from ground is constant at 285.18 ± 0.08 eV while referenced to the FL. *This result could not be reproduced in our experiments for any charge neutralizer setting.* The only possibility for constant C 1s position seems to occur if the specific conditions of charge neutralizer current are used as indicated by the crossover point in Fig. 1(a). However, this would <u>not</u> give the constant C 1s peak position referenced to sample FL, as shown in Fig. 1(c). What adds to the confusion is that Ref. 14 states that "An analysis of an Al foil only area on the floated sample gave an AdC C 1s value of 285.8 eV when corrected to the (now Al metal only) Fermi level. The uncorrected C 1s peak is still in a similar position to the mixed Au/Al C 1s spectra." It is therefore unclear if the data shown in Fig. 9 of Ref. 14 are in fact corrected to FL values from the respective scans and what else could be the reason for significantly higher BE obtained from the Al-only part of the sample (provided that all data shown in Fig. 9 are referenced to the FL).

3.2. Is differential charging responsible for C 1s peak shifts from the "recommended" 284.8 eV?

It was suggested in Ref. 14 that differential charging in a surface oxide layer may be responsible for shifts of the C 1s peak from AdC
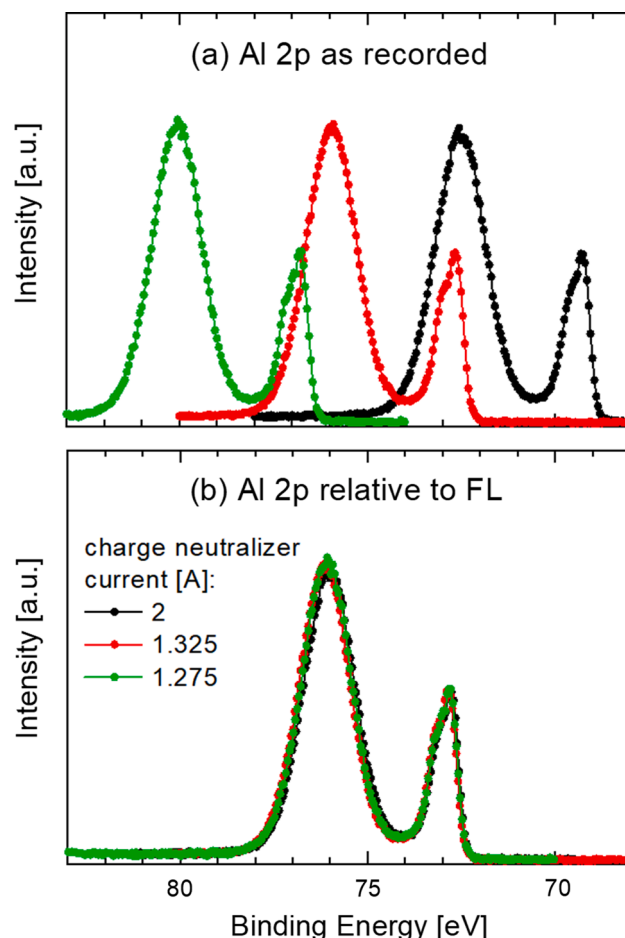
layers accumulating on thin films as the samples reported in our previous paper (Ref. 9) were stored in air for prolonged period of time (several weeks to a few years). The insulating character of the native oxide was thought to cause a potential drop of up to 2 V over a few nm thick oxide layer, which made the C 1s peaks of AdC layer sitting on top of the oxide, appear shifted to higher BE. In the case of the Al and Au foils considered in Ref. 13, the required potential drop would need to amount to 1.5 V over the few nm thick Al oxide, to account for the 1.5 eV shift of the C 1s peak on the Al foil with respect to that on Au. We performed several experiments to evaluate this possibility and our findings are presented in the item-by-item manner below.

3.2.1. Al 2p spectra recorded from the Al foil are independent of the surface potential

As shown in Fig. 4, the BE difference between the metal and the oxide components in the Al 2p spectra is independent of the surface potential that is varied from −3.97 V to + 3.51 V by adjusting the charge neutralizer current. Moreover, *spectra recorded under so different surface charge state conditions are identical.* If the Al oxide layer was in fact positively charged with respect to the underlying Al metal under conventional conditions (samples in electrical contact with the spectrometer) one would expect this charge to be completely neutralized, while using neutralizer settings that are sufficient to reach the overcompensation (negative surface potential, in this case obtained for $I_N >$ 1.325 A). This should result in a pronounced shift of the oxide peak

towards the metal peak by ca. 1.5 eV, hence, a significantly different Al 2p spectrum should be obtained. This is clearly not the case in our experiments as evidenced by Al 2p spectra in Fig. 4.

3.2.2. Al 2p spectra from the Al foil are independent of the x-ray power

Another way to alter the surface charging state in the case of measurements performed with samples electrically isolated from the sample holder is to vary the photoelectron current by means of altering the x-ray power. Lower current means lower voltage drop over the insulating surface oxide, hence lower BE values for the oxide peak with respect to that of a metal peak are expected. We performed this experiment in two configurations: with the Al foil either in good electrical contact to the sample holder or electrically isolated from the spectrometer. In the first case (see Fig. 5(a)) a gradual decrease of signal intensity takes place as the x-ray power is reduced from 150 to 15 W. An order of magnitude change has no effect on the oxide – metal peak splitting in the Al 2p spectra.

In the second case (see Fig. 5(b)) the x-ray power is varied from 225 to 15 W, while the neutralizer current setting is at 1.325 A, which corresponds to nearly neutral surface with our standard power setting of 150 W (cf. Fig. 1(b)). The surface is charged positively for x-ray power settings higher than 150 W, as the neutralizing electron flux is too low to compensate charge loss resulting from higher photoelectron currents. The opposite is true for x-ray power lower than 150 W, in which case the surface is negatively charged. Again, there is no significant change in the

BE splitting between the oxide and metal peaks in the Al 2p spectrum, which speaks against the idea of differential charging in the present Al oxide layer.

3.2.3. Separation between metal and oxide peaks in Al 2p spectra from the Al foil is independent of the oxide thickness

If differential charging were taking place in the top oxide layer it is reasonable that the effect would scale with the oxide thickness. To test that hypothesis, we recorded Al 2p spectra from an Al foil that was first sputter-etched to remove the original oxide and then exposed to various environments for controlled amounts of time to monitor the oxide peak position as a function of oxide thickness. The latter is estimated from relative signal intensities using the well-known formula of Strohmeier. [19] Results shown in Fig. 6 reveal that the BE of the oxide peak does not vary by more than 0.1 eV for an Al oxide thickness ranging from 0.7 to 4.7 nm. The C 1s peak position is confirmed at 286.40 ± 0.16 eV independent of Al oxide thickness. This observation clearly disproves the hypothesis that differential charging in the Al oxide layer causes the shift of the oxide peak (and the C 1s peaks of the AdC layer) for the oxide thickness not exceeding 5 nm.

Under the present experimental condition, the inelastic mean free path for Al 2p electrons in Al is 2.8 nm, [20] which is 4 times longer than the minimum Al oxide thickness shown in Fig. 6. It is hard to envision that under such circumstances the surface of the oxide would develop the positive potential of 1.5 V.

In order to develop a positive surface potential resulting in significant shift of the Al oxide peak, the oxide thickness has to significantly exceed the electron inelastic mean free path so that the photoelectrons originating from the underlying Al metal can no longer reach the oxide surface and prevent buildup of the positive charge. This is well illustrated in the paper by Baer et al. who reported Al 2p spectra from samples with the oxide thickness varying from 6.2 to 36 nm [21]. The oxide peak for the sample with the thinnest oxide layer was at 75.7 eV, i. e., essentially the same binding energy as shown in Fig. 6. For samples with thicker oxide layers (22 and 36 nm) the Al 2p peak was clearly shifted towards higher binding energy (along with C 1s peak of AdC). The comparison of our data shown in Fig. 6 with those reported by Baer et al. suggests that the buildup of the positive charge in the Al oxide (evidenced by the oxide peak shift to higher binding energy) starts to be noticeable for oxide thickness exceeding 6 nm, i.e., well above the thickness range relevant for the present experiments. For those thicker
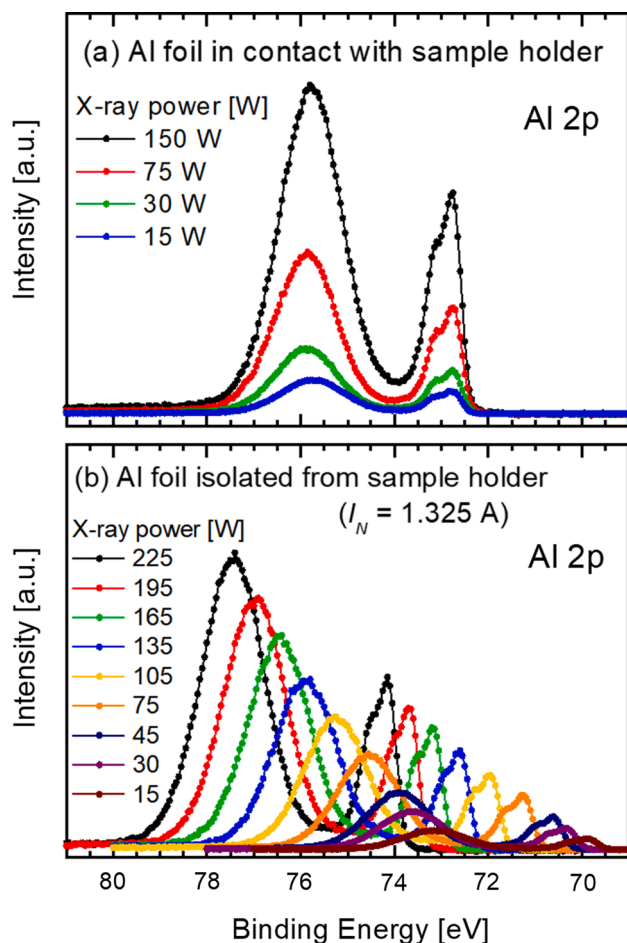

Fig. 5. Al 2p spectra from the Al foil acquired as a function of x-ray power for (a) sample in good electrical contact to the sample holder, and (b) sample electrically isolated from the spectrometer. In the latter case the neutralizer current setting is at 1.325 A, which corresponds to nearly neutral surface with the standard anode power setting of 150 W.
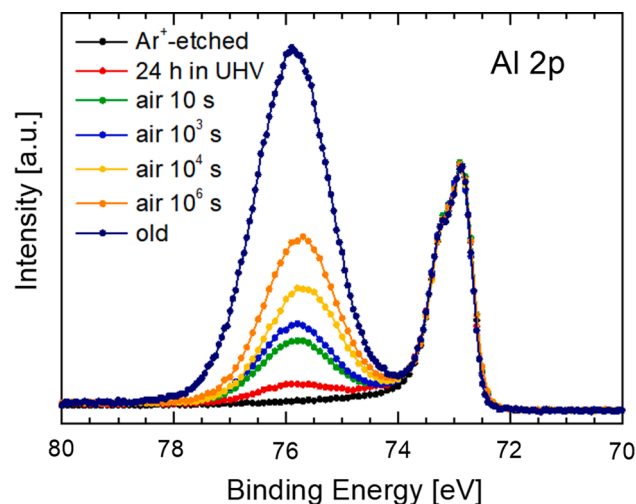

Fig. 6. Al 2p spectra from an Al foil (in contact with spectrometer) that was first sputter-etched to remove the original oxide (spectrum marked as "Ar+-etched") and then exposed to either UHV (spectrum denoted as "24 h in UHV") or laboratory air for times ranging from 10 to 10^6 s. Spectrum marked as "old" is acquired from a non-treated Al foil.

oxide layers, charging issues most certainly play a role in the measurement of the C 1s BE for AdC (in addition to shifts caused by the VL alignment). Considering that the oxide film thickness is often unknown, one cannot determine the true reason for C 1s peak shifts unless the in-depth analysis (e.g., by analyzing samples with varying oxide thickness as we have done here for the case of Al oxide – see Fig. 6) is performed.

3.2.4. The oxide peak in Al 2p spectrum from an Al foil does not have a shape that would suggest differential charging

According to claims made in Ref. 14 the 1.5 eV difference in the C 1s peak position between Au and Al foils is caused by the voltage drop over the Al oxide. The implication of that is that the Al 2p signal from the oxide volume closest to the oxide/metal interface should appear shifted by 1.5 eV to lower binding energy with respect to that from the oxide surface. As the oxide layer thickness (0.7–4.7 nm) is shorter than the XPS probing depth (8.4 nm for Al 2p electrons excited with the Al Kα source) one would expect the see a tail on the low BE side of the Al 2p oxide peak due to the 1.5 V voltage drop over the oxide. No such features have been observed in any of our experiments described above, nor in Ref. 14.

3.2.5. The C 1s peak position correlates with the sample work function

We have shown previously for nearly hundreds of thin film samples that the measured BE of the C 1s peak of AdC correlates well to the sample work function such that the sum of both is nearly constant at 289.58 ± 0.14 eV [9]. This result indicates vacuum level alignment at the AdC/sample interface, which is typical for weakly-interacting materials, where charge transfer across the interface, necessary for FL alignment, does not takes place. [22] The case of adventitious carbon appears analogous to thin organic layers deposited on metals by *ex-situ* techniques such as spin-coating. [23] Contacts for these samples often remain within the Schottky-Mott limit, with the electronic levels of the adsorbate being determined by the substrate work function. [24] In the case of Au and Al foils, the work function difference assessed by UPS from the same samples as used for XPS analyses is 1.5 eV, i.e., exactly matching the shift between C 1s peaks from AdC layers accumulating on these two surfaces. If, as suggested in Ref. 14, differential charging in oxide layers was responsible for C 1s peak shifts no such correlation is expected.

3.2.6. In many cases C 1s peak shifts to BE lower than 284.8 eV

The hypothesis of differential charging in the native oxide being responsible for the C 1s peaks shifts [7,8,9,13] faces serious problems concerning samples that exhibit shift towards BE lower than the "recommended" value of 284.8 eV. Several examples from Ref. 9 include: VN (C 1s peak at 284.15 eV), MoN (C 1s peak at 284.08 eV), or WN (C 1s peak at 284.22 eV). Such low BE values for C 1s peaks of AdC are, however, easily explained within the VL-alignment interpretation. [9,13] All such samples exhibit relatively high work function values − 5.16 eV for VN, 5.35 eV for MoN, and 5.23 eV for WN. Thus, to maintain the $E_B^F + \phi_{SA}$ sum constant at ∼ 289.6 eV, the respective C 1s peaks need to appear at lower BEs. The resulting C 1s BE values with respect to the VL are then roughly constant at 289.31 eV for VN, 289.43 eV for MoN, and 289.45 eV for WN.

3.2.7. C 1s peak shifts are also observed for Ar⁺-etched samples exposed to the UHV environment

One of the claims brought forward in Ref. 14 is that C 1s shifts are caused by uncontrolled differential charging that develops in the native oxide layer as samples have been exposed to air for long times (weeks to years). However, in our first paper on this topic [7] we reported a 1.44 eV difference in the C 1s peak position for a series of TM nitride thin film samples exposed to air for no more than 10 min. Also in that case, very good correlation between the C 1s peak position and the sample work function was found.

Crist reported C 1s peak positions for several substrates that were

stored in UHV for at least 10 h following the Ar⁺ sputter-etch applied to remove native oxides.[10] In this data set, the C 1s binding energy varied from 284.2 eV for Pd to 286.7 eV for Y. This 2.5 eV difference in the C 1s peak position fully supports our observations and stands out in contrast to the claims of a constant binding energy of the C 1s peak of adventitious carbon.

Moreover, as stated in Sec. 3.2.3 the BE of the C 1s peak for AdC on the Al foil is fairly independent of the native oxide thickness (confirmed for the oxide range from 0.7 to 4.7 nm).

We encourage all XPS practitioners to sputter-etch Al and Au foils and record C 1s peak position after storage in UHV and/or exposure to air for controlled amounts of time. Such experiments are easily done in almost every XPS laboratory.

3.2.8. C 1s peak splitting of 1.5 eV between spectra recorded from Al and Au foils is observed irrespective of the surface potential

Results shown in Fig. 1(c) show a constant shift of 1.5 eV between C 1s peaks from AdC layers on Au and Al foils. This is irrespective of how the measurement is performed: samples in contact with the spectrometer or samples isolated. In the latter setup the splitting is shown to be independent of the surface potential (controlled by charge neutralizer current). The latter result contrasts with what was observed in Ref. 14 (Fig. 9). Unfortunately, no results from experiments performed with both samples in contact to the sample holder were reported in that paper.

3.2.9. Splitting between oxide and metal peaks in Al 2p spectrum from Al foil is consistent with other reports

In our measurements performed with samples in contact with the spectrometer, the oxide peak in the Al 2p spectrum from an Al foil appears at 75.8–76.0 eV. A lower value for the oxide peak in the Al 2p spectrum of 74.8 eV was reported in measurements performed with samples isolated from ground [14]. In that paper it is claimed that this lower BE value is an "accepted value" for the BE of an Al 2p oxide peak and that it is lower since differential charging is avoided by isolating samples from ground. First of all, the NIST data base shows values for the Al oxide peak that vary by 3 eV, so it is difficult to assert what the "correct value" would be [18]. Secondly, as illustrated in Figs. 3-5, smaller splitting between metal and oxide peaks could not be reproduced in any of our experiments, no matter if samples were grounded or isolated from the spectrometer. Thirdly, the 3.0 eV splitting between metal and oxide peaks in Al 2p spectra acquired from an Al foil and reported in our earlier paper [13] does not stand out as an exceptionally high value. For example, Baer et al. report the difference between Al 2p metal and Al oxide peaks in the range 2.7–2.9 eV, [25] depending on whether spectra are recorded with samples grounded or isolated from ground and neutralizer. Crist published an Al 2p spectrum from an Al foil with the oxide peak at 75.7 eV, hence resulting in the 2.8 eV splitting. [26]

Therefore, we suggest that the difference between our results and those reported in Ref. 14 is more likely due to the fact that the chemical identity of the compound being studied is not the same. Al oxides can very well be substoichiometric, or even be hydroxides. Quantitative analysis in our case reveals the O/Al-oxide ratio of 1.6, thus somewhat overstoichometric oxide. This result could potentially explain the larger BE separation from the metal peak (on average less negative charge per O atom than in stoichiometric Al_2O_3).

4. Summary and conclusions

In order to evaluate the potential role of differential charging in the native Al oxide on the binding energy of C 1s peaks of adventitious carbon accumulating on Al foils we performed a series of experiments with samples electrically isolated from the spectrometer. We varied the charge neutralizer current to record spectra with the surface in the electrically neutral state, as well as over- and under-compensated.

Markedly, for any flood gun setting (spanning from an under- to an overcompensated surface), the positions of C 1s peaks from Au and Al foils are constant with respect to their Fermi levels at 284.80 ± 0.05 eV and 286.31 ± 0.06 eV, respectively. Thus, the present experimental evidence fully supports the findings presented in our previous papers (experiments performed in the conventional way with samples connected to the spectrometer), that the binding energy of C 1s peaks from Au and Al foils differs by 1.5 eV. The prevailing physical interpretation of this difference is the vacuum level alignment at the AdC/sample interface, which makes the BE of the C 1s peak steered by the sample work function such that the sum of both is constant at ~ 289.6 eV.

Moreover, the energy separation between metal and oxide peaks in Al 2p spectra from an Al foil is independent of the surface potential when varied from -3.97 V to $+3.51$ V by adjusting the charge neutralizer current. In addition, the peak separation shows no dependence on the photoelectron current (varied by adjusting the x-ray power) and the Al oxide thickness (in the range from 0.7 to 4.7 nm). All these observations contradict the notion of differential charging taking place in these thinner Al oxide layers with the thickness in the same range as the electron inelastic mean free paths, thus allowing for efficient neutralization of the surface charge by substrate electrons. It is, however, important to note that one should not extrapolate this result to any type of samples. It is well-known that differential charging develops in thicker oxide layers,[21] which certainly has an influence on the BE of the C 1s peak from AdC (in addition to the work function effect). Thus, one cannot determine the true reason for C 1s peak shifts before conducting the in-depth analysis, e.g., by analyzing samples with varying oxide thickness (cf. Fig. 6).

While differential charging is a well-proven phenomenon for non-homogeneous samples composed of phases of low and high conductivity, it should not be used as a general explanation to interpret BE shifts that are otherwise difficult to explain. It certainly fails to explain observations of good correlation between the C 1s peak position and the sample work function [9], as well as the fact that in many cases the measured BE of the C 1s peak is lower than the "recommended" value of 284.8 eV. Having said that, we do not claim that the vacuum level alignment condition holds for each and every sample type and under any circumstances. Other phenomena like surface dipoles, surface states, differential charging included, can certainly disrupt VL alignment adding complexity to the binding energy reference problem in XPS.

In the context of using C 1s peak for charge referencing the true origin of C 1s peak shifts is, however, a secondary issue. The experimental evidence shows that the binding energy of the C 1s peak of AdC varies by as much as 2.6 eV with respect to the sample Fermi level, hence, it cannot serve the purpose of an internal energy reference.

CRediT authorship contribution statement

G. Greczynski: Conceptualization, Investigation, Funding acquisition, Writing – original draft. **L. Hultman:** Writing – review & editing, Funding acquisition.

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.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2022.154855.

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