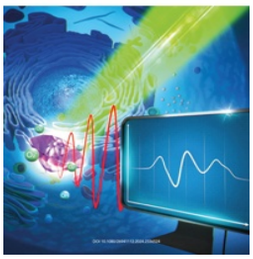
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REVIEW ARTICLE

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Critical review of band offset determination by X-ray photoelectron spectroscopy for the heterojunctions on diamond substrates

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ABSTRACT

Valence band offsets (VBO) of heterojunctions can be determined by X-ray photoelectron spectroscopy (XPS) directly. XPS VBO determinations for heterojunctions on diamond substrates have been reported by many workers for the last decades. We have reviewed these reports critically and found that none of the results of these reports are rigorous enough, and that most of the results are incorrect. The reasons for this are the following three. First, most of the researchers working on diamond devices are not aware of the fact that the top of valence band (VB) does not coincide with an extrapolation point of leading edge in VB XPS spectrum. It is important to note the special nature of diamond valence band. Second, most of the researchers working on diamond devices are not aware of the fact that the *ex-situ* samples normally used in XPS measurements are covered with adventitious carbon-containing molecules. This prevents the identification of C 1s XPS peak from the substrate diamond. Third, morphology of sample surfaces is rarely examined. It is notable that the probing depth of XPS is so small (~ 2 nm) that the sample surface must be uniform in an atomistic scale of ~0.2 nm.

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Band offset; heterojunction; X-ray photoelectron spectroscopy; valence band; diamond devices; carbon 1s

1. Introduction

Heterojunctions on diamond substrates are often used in diamond-based electronic devices. Information about the band offset in heterojunction is important in designing and understanding the performance of the electronic devices and it is often obtained by X-ray photoelectron spectroscopy (XPS). To the author's knowledge, there have been almost 20 literatures [1–19] that report band offset determination by XPS in heterojunctions on diamond substrates for the last decades as summarized in Tables 1–3. The way they used XPS in band offset determination was mostly wrong and came to wrong conclusions. We would like to explain the right way based on our recent publications [20,21] and unveil how the others are wrong.

2. Principle of valence band offset determination by XPS

Figure 1 shows schematic illustration of a cross-sectional view of photoelectron detection from a heterojunction on diamond substrate used for valence band offset (VBO) determination by XPS. Figure 2 shows schematic illustration of relevant energy-levels at the heterojunction. Equation (1) shows formula for the evaluation of VBO (ΔE_V) by XPS [20]. The energy scale in Figure 2 is defined as binding energy (E_B) with respect to a reference energy (E_{RF}). It is to be noted that photoelectron spectrometer used must be well calibrated by standard metallic samples of Au, Ag, and Cu [22]. It is common that a commercial photoelectron spectrometer is calibrated in a reasonable accuracy of $\leq \pm 0.2$ eV. It is also noted that the total energy resolution used must be reasonably good at around 0.5 eV.

$$\begin{aligned}\Delta E_V &\equiv E_{V_SM} - E_{V_Dia} \\ &= E_{core_SM} - \left(E_{core_SM} - E_{V_SM}\right) - E_{C1s_Dia} + \left(E_{C1s_Dia} - E_{V_Dia}\right) \\ &= \left[E_{core_SM} - E_{C1s_Dia}\right]_{\text{Measured}} + \left[E_{C1s_Dia} - E_{V_Dia}\right]_{\text{Material Constant}} \\ &\quad - \left[E_{core_SM} - E_{V_SM}\right]_{\text{Material Constant}}\end{aligned} \tag{1}$$

The second material (SM) appearing in Figures 1 and 2 and Eq. (1) is the material that forms the heterojunction on diamond and its thickness has to be 2 ~ 3 nm in order to have XPS sensitivity both from substrate diamond and SM. The thickness of SM must be uniform without island-formation; the roughness (average roughness *Ra*) of SM and substrate surfaces must be small enough to be $Ra \leq 0.2$ nm. The reference energy (E_{RF}) can be the Fermi level (E_F) when SM and substrate diamond are conducting. When the sample is electrically connected to a metallic sample holder, E_{RF}

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Table 1. Summary of VBO XPS studies for ALD Al_2O_3 layers on hydrogen-terminated diamond.

Reference	Substrate diamond	About photoelectron spectrometer, light source, detection angle, energy resolution, etc.	Sample holding method and use of charge-neutralizer	Method of E_{V_dia} determination	Value of E_{C1s_Dia}-E_{V_dia} (eV)	Second material, (thickness in nm)	Sample surface roughness	Identification of diamond C 1s peak	Reported valence band offset (eV)
1	Hydroge-terminated CVD diamond on Ib substrate (100)	Commercial spectrometer, monochromated Al K_α source, detection angle and energy resolution not specified	Not specified	Extrapolation of leading edge	283.1	ALD Al_2O_3 (4 nm)	Not specified	Not explained. Likely to be adventitious C 1s	2.96 ± 0.2
4	NO_2 exposed hydrogen-terminated CVD diamond on IIa (100)	Synchrotron radiation. hv = 700 and 60 eV; Resolution 0.78 and **0.04** eV for core-level and valence band measurements, respectively. Detection angle not specified.	Not specified	Onset point of spectrum	284.3	ALD Al_2O_3; **depth profile measurements by Ne^+ sputtering**	Not specified	C 1s peak after Ne^+ ion etching	3.9
7	Hydrogen-terminated boron-doped p-type (111) diamond and phosphorus-doped n-type (111) diamond	Commercial spectrometer, monochromated Al K_α source, detection polar angle at ~0°, an energy resolution of ~0.5 eV	Conductive carbon-tape was attached to diamond surface. Au pads were attached on the sample surface. Charge-neutralizer was not used.	Extrapolation of leading edge	282.2 ± 0.4 eV for p-type, 282.9 ± 0.4 eV for n-type	ALD Al_2O_3, 2 nm for n-type and 3 nm for p-type diamond	Not specified	Peak positions of C 1s spectra were assumed to be from diamond	1.8 ± 0.2 on (111)p and 2.7 ± 0.2 on (111)n
9	Hydrogen-terminated lightly B-doped CVD diamond on IIa (100)	Commercial spectrometer, monochromated Al K_α source, **in-situ measurments,** detection polar angle not specified, an energy resolution of ~0.3 eV	Not specified	Assumed to be at zero binding energy	284.1 ± 0.1	PE-ALD Al_2O_3 (1–2 nm): **Applied H-plasma treatments**	Not specified	Peak position of C 1s spectra was assumed to be from diamond	2.7
10	NO and SO_2 exposed hydrogen-terminated CVD diamond on Ib (100)	Synchrotron radiation. hv = 700 and 60 eV; Resolution 0.78 and **0.04** eV for core-level and valence band measurements, respectively. Detection angle not specified.	Not specified	Onset point of spectrum	284.21 for NO exposed and 284.19 for SO_2 exposed	ALD Al_2O_3; **depth profile measurements by Ne^+ sputtering**	Not specified	C 1s peak after Ne^+ ion etching	3.7 for NO exposed and 3.5 for SO_2 exposed
11	Hydroge-terminated CVD polycristalline diamond	Commercial spectrometer, monochromated Al K_α source, detection angle and energy resolution not specified	Not specified	Extrapolation of leading edge	Not reported	ALD Al_2O_3, 4 nm	Not specified	Not reported but it seems that the highest peak position of C 1s spectra was assumed to be from diamond	3.28
14	hydrogen-terminated B-doped & non-doped CVD diamond on IIa (100)	Commercial spectrometer, monochromated Al K_α source, **in-situ measurments**, detection polar angle = 0 deg., an energy resolution of ~0.3 eV	Not specified	Assumed to be at zero binding energy	284.1 ± 0.1	PE-ALD Al_2O_3 (2,4 nm), MoO_3 (2 nm): **Applied H-plasma treatments**	Not specified	Peak position of C 1s spectra was assumed to be from diamond	2.6 for Al_2O_3, 3.1 for MoO_3

The contents that are not satisfactory in terms of VBO XPS evaluation are singly underlined. The contents that are related to special procedures are shown in bold characters.
CVD: Chemical vapor deposition; ALD: Atomic layer deposition; PE-: Plasma enhanced.

Table 2. Summary of VBO XPS studies for ALD Al_2O_3 layers on oxygen-terminated diamond.

Reference	Substrate diamond	About photoelectron spectrometer, light source, detection angle, energy resolution, etc.	Sample holding method and use of charge-neutralizer	Method of E_{V_dia} determination	Value of E_{C1s_Dia}-E_{V_dia} (eV)	Second material, (thickness in nm)	Sample surface roughness	Identification of diamond C 1s peak	Reported valence band offset (eV)
5	Oxygen-terminated lightly B-doped on heavily B-doped CVD diamond on Ib(100)	Commercial spectrometer, monochromated Al K_α source, detection angle and energy resolution not specified	Not specified	Extrapolation of leading edge	282.25	ALD Al_2O_3 (2 nm)	Not specified	Not explained how they are identified. C-Al C 1s component should be much weaker than substrate diamond C 1s	1.43 ± 0.2
12	Oxygen-terminated lightly B-doped CVD diamond on Ib(100)	Commercial spectrometer, monochromated Al K_α source, detection angle and energy resolution not specified	Not specified	Onset point of spectrum	283.9	ALD Al_2O_3: **depth prifile measurments by Ar^+ spurtering**	Not specified	C 1s peak after Ar^+ ion etching	3.4 ± 0.2
18	Oxygen-terminated lightly B-doped CVD diamond on Ib(100)	Commercial spectrometer, monochromated Al K_α source **(scanning micro-beam)**, detection polar angle at ~45°, energy resolution not specified correctly	Not specified but **a net-patterned gold (Au) mask was deposited on the surface.**	Extrapolation of leading edge	283.65	ALD Al_2O_3 (3 nm)	Not specified	Highest peak position of C 1s spectra was assumed to be from diamond. Second highest C 1s peak was assigned to C-B bond, which is impossble for the lighly B-doped substrate.	1.30

The contents that are not satisfactory in terms of VBO XPS evaluation are singly underlined. The contents that are related to special procedures are shown in bold characters. CVD: Chemical vapor deposition; ALD: Atomic layer deposition.

coincides to E_F of the sample holder. For insulating SM and insulating substrate diamond, electrical connection to the sample holder is not possible and thus we must use a charge-neutralizer in XPS measurement. In this case, E_{RF} can be zero binding energy and would be close to E_F of the sample holder, but not necessarily equal to E_F. The principle of Eq. (1) relies on the fact that E_{C1s_Dia}-E_{V_Dia} and E_{core_SM}-E_{V_SM} are the material constant and thus $[E_{core_SM} - E_{C1s_Dia}]_{Measured}$ gives ΔE_V. This principle is simple and first applied by Waldrop and Grant for AlN/GaN (0001) heterojunction with monochromatic Al K_α excitation source [23]. The principle is in fact based on the fact that the energy difference between VBM and certain core level is a material constant both for the second material (AlN) and the substrate (GaN). This is the same for diamond substrates but the determination of VBM needs special care for the substrate as explained below.

Carbon 1s level is the only core-level that exists in the substrate diamond and the material constant of E_{C1s_Dia}-E_{V_Dia} is 284.0 ± 0.12 eV as determined by a precise and elaborated XPS study [24]. Similar value of E_{C1s_Dia}-E_{V_Dia} = 283.9 ± 0.1 eV is obtained by angle-resolved synchrotron radiation photoelectron spectroscopy combined with XPS [25]. To the author's knowledge, these are the only reports that studied E_{C1s_Dia}-E_{V_Dia} precisely and correctly. The value 284.0 ± 0.12 eV plays a very important role in XPS band-offset determination. We find that in most of the literatures in Tables 1–3, they used wrong values for this. This is because E_{V_Dia} is evaluated from the extrapolation point of leading edge of diamond valence band XPS spectra. This procedure is usually correct for most materials, but this is *wrong for diamond*. In Figure 3, valence band XPS spectra of oxygen-terminated boron-doped diamond(100) sample is reproduced from Figure 6 in Ref. [24]. The extrapolation point of leading edge gives point B (E_B =1.30 eV), while the actual and correct E_{V_Dia} exists at point A (E_B = 0.65 eV). The difference in E_B between A and B points is 0.65 eV. (If the extrapolation is made in a larger energy scale of ~4 eV, the difference is even larger to be ~1. 0 eV as seen later in Tables 1–3. Specifically, refer to diamond valence band spectra of Figure 1(b) of Ref. [1], Figure 5 (a) of Ref. [8], and Figure 2(b) of Ref. [11]. This error in E_{C1s_Dia}-E_{V_Dia} evaluation is directly reflected in VBO evaluation as Eq. (1) shows). This is because that the symmetry character at E_{V_Dia} of diamond is very special in that photoionization cross section by Al K_α excitation source is very reduced to have weak features at E_{V_Dia} [26]. Koh et al. [27] claimed that E_{C1s_Dia}-E_{V_Dia} =282.8 eV and that E_{C1s_Dia}-E_{V_Dia} values in the range of 284 eV are inflated due to the exact position of E_{V_Dia} being obscured by the presence of sp^2 carbon related surface states above E_{V_Dia}. This argument is simply phenomenological without paying attention to the symmetrical character of diamond valence band. If the claimed E_{C1s_Dia}-E_{V_Dia} = 282.8 eV were correct, E_{V_Dia} values for conducting diamond

Table 3. Summary of VBO XPS studies for second materials other than Al_2O_3 layers on diamond substrate.

Reference	Substrate diamond	About photoelectron spectrometer, light source, detection angle, energy resolution, etc.	Sample holding method and use of charge-neutralizer	Method of E_{V_dia} determination	Value of E_{C1s_Dia}-E_{V_dia} (eV)	Second material, (thickness in nm)	Sample surface roughness	Identification of diamond C 1s peak	Reported valence band offset (eV)
1	Hydrogen-terminated CVD diamond on Ib substrate (100)	Commercial spectrometer, monochromated Al K_α source, detection angle and energy resolution not specified	Not specified	Extrapolation of leading edge	283.1	HfO_2 (4 nm)	Not specified	Not explained. Likely to be adventitious C 1s	2.66 ± 0.2
2	Hydrogen-terminated CVD diamond on Ib substrate (100)	Commercial spectrometer, monochromated Al K_α source, detection angle and energy resolution not specified	Not specified	Extrapolation of leading edge	283.1	SD $LaAlO_3$ (2nm) on ALD Al_2O_3 (4.3 nm)	Not specified	Used previous work of Ref.1 and Al 2p and La 3d core levels	4.0 ± 0.2 for $LaAlO_3$
3	Hydrogen-terminated CVD diamond on Ib substrate (100)	Monochromated Al K_α source, detection angle and energy resolution not specified for main case	Not specified	Extrapolation of leading edge	283.1	RF sputterred Ta_2O_5 (2 nm)	Not specified	Not explained. Likely to be adventitious C 1s	1.5 ± 0.2
6	Hydrogen-terminated CVD diamond on Ib substrate (100)	Commercial spectrometer, monochromated Al K_α source, detection angle and energy resolution not specified	Not specified	Extrapolation of leading edge	283.1	SD ZrO_2 (2nm) on ALD Al_2O_3	Not specified	Used previous work of Ref.1 and Al 2p and Zr 3d core levels	2.3 ± 0.2
8	Hydrogen-terminated CVD diamond on off-cut (0.2° and 2.0°) Ib substrate (111)	Commercial spectrometer, monochromated Al K_α source, detection polar angle not specified, an energy resolution of ~0.5 eV	Not specified	Extrapolation of leading edge	282.8	MOVPE AlN (5 nm)	Not specified	Peak position of C 1s spectra was assumed to be from diamond	~2.0
13	Oxygen-terminated lightly B-doped CVD diamond on Ib(100)	Monochromated Al K_α source, detection angle and energy resolution not specified correctly. **Performed a mild Ar^+ cleaning of sample.**	Not specified	Extrapolation of leading edge	283.1	ALD SiO_2 (2 nm)	Not specified	Main deconvoluted peak position of C 1s spectra was assumed to be from diamond	2.0
15	Polished polycrystalline diamond	Commercial spectrometer, monochromated Al K_α source, detection angle and energy resolution not specified	Not specified	Extrapolation of leading edge	282.96	ALD Ga_2O_3 (80 nm): **depth prifile measurments by Ar^+ spurtering**	RMS roughness: ~0.18 nm on Ga_2O_3, 0.51 nm on diamond substrate	Assumed highest C 1s peak after Ar^+ ion etching	1.18
16	CVD grown polycrystalline diamond with facets of (111), (220), (311) and (400)	Commercial spectrometer, monochromated Al K_α source, detection angle and energy resolution not specified	Not specified	Extrapolation of leading edge	282.9	IBSD h-BN : **depth prifile measurments by Ar^+ spurtering**	RMS roughness: ~0.5 nm on h-BN, ~1 nm on diamond substrate	Assumed highest C 1s peak after Ar^+ ion etching	2.08
19	Ib(100)-type diamond, no other description	Monochromated Al K_α source, detection polar angle not specified, an energy resolution of ~0.5 eV	Not specified	Extrapolation of leading edge	283.33	PLD β-Ga_2O_3 (3 nm)	RMS roughness: ~33.1 nm on Ga_2O_3, 1.58 nm on diamond substrate	Highest peak position of C 1s spectra was assumed to be from diamond.	1.41

The contents that are not satisfactory in terms of VBO XPS evaluation are singly underlined. The contents that are related to special procedures are shown in bold characters.
CVD: Chemical vapor deposition; ALD: Atomic layer deposition; SD: Sputter deposition; MOVPE: Metal-organic vapor phase epitaxy; IBSD: Ion beam sputter deposition; EBD: Electron beam deposition; PLD: Pulsed lazer deposition.

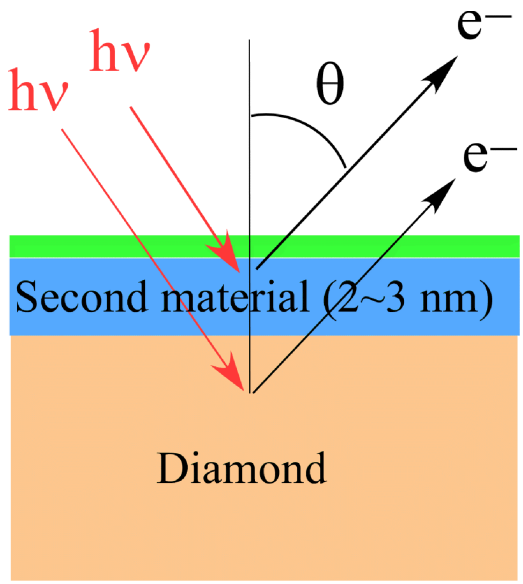


Figure 1. Schematic illustration of a cross-sectional view of photoelectron detection from a heterojunction on diamond substrate. The green part above the second material indicates an adventitious carbon layer for an *ex-situ* sample.

samples would be all unphysically large at about 1.3 Ev [20,28].

It may be worthwhile to explain further how special the symmetry character of diamond valence band is. McFeely et al. [26] reported comparison (Figure 2 of [26]) for diamond of VB XPS spectrum, K x-ray emission spectrum, and calculated density of states. From the comparison, they obtained a fractional 2p-character distribution curve (Figure 5 of [26]) over the diamond valence band and found that fractional 2p-character is 92% at VBM. It was reported [26] that the photoelectron cross-section ratio of C 2p to C 2s by Al K_α excitation source is ~1/13 referring to [29]. It was in reality the cross-section by Mg K_α excitation source and the reported values were preliminary [29]. It was later reported theoretically [30] that photoelectron cross-section ratio of C 2p to C 2s by Al K_α excitation source is ~1/31, which is really small. Therefore, we expect very weak XPS features at VBM of diamond. McFeely et al. [26] wrote that it was necessary to expand the density of states curve to match the XPS spectrum near VBM which might have resulted in the loss of some meaningful fine features. They did not examine the fine structures of XPS spectrum at VBM. The fine structures were indeed examined in Ref. [24] and shown in Figure 3 as above. From a comparison with the Fermi edge spectrum (Figure 4 of Ref. [24]) of a reference Au metal, it is clear that the weak feature appearing at 1 eV in Figure 3 is real, not an artifact such as a finite-resolution tail. It may be worthwhile to note further that the previous report [31] by the same group of [26] reported that VBM can be obtained by extrapolating the steepest part of leading edge of VB spectrum. This in fact appeared to be wrong as shown above.

The energy ($h\nu$) of photo-excitation source must be large enough to have a large probing depth comparable to the thickness of SM. Most common photo-excitation source is monochromatized Al K_α line at $h\nu$ = 1486.6 eV. C 1s photoelectrons excited by Al K_α line in the substrate diamond have a kinetic energy of ~1200 eV and must path through the SM layer and the adventitious carbon layer for *ex-situ* sample. This causes intensity dumping due to inelastic scattering on its way out and the mean free path of no-energy-loss electrons is comparable to the thickness of SM. The XPS measurements are usually performed *ex-situ*, thus the sample has adventitious carbon--containing molecules on the SM surface and gives main component of C 1s spectra. We must distinguish diamond C 1s from adventitious C1s. In most of the literature in Tables 1–3, they gave less attention to this point as will be described later. The most common method of distinguishing diamond C 1s from adventitious C1s is the change in surface-sensitivity in XPS measurements. This is mostly

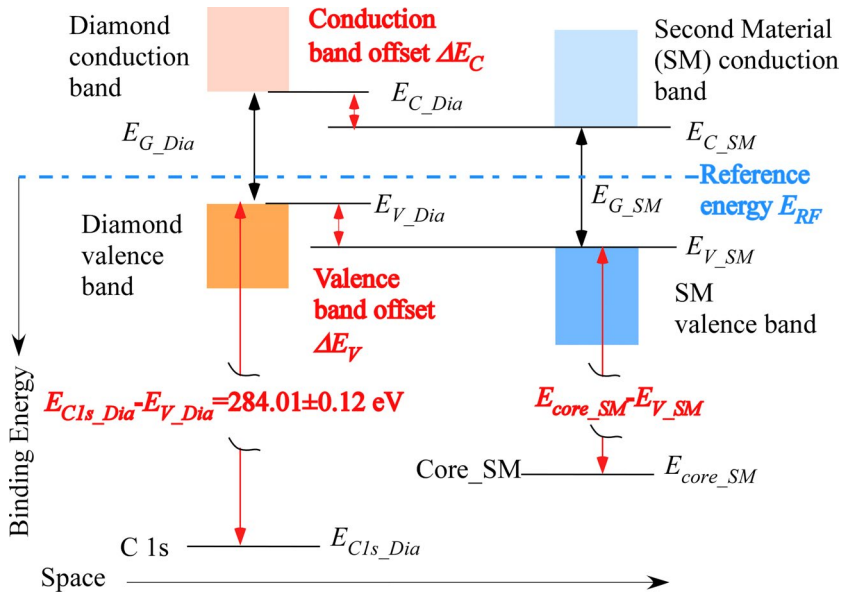


Figure 2. Schematic illustration of relevant energy-levels at the heterojunction on diamond substrate.

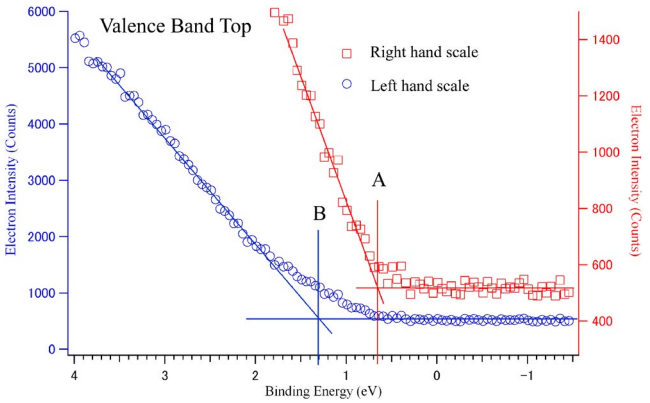


Figure 3. Valence band XPS spectra of oxygen-terminated boron-doped diamond(100) reproduced from Figure 6 of Ref. [24]. (Reprinted with permission of IOP publishing on behalf of JSAP under license ID 1682761-1.)

performed by changing the electron detection polar angle θ (cf. Figure 1): The larger θ is, the larger the surface sensitivity is. In Figure 4, we showed C 1s spectra reproduced from Figure 6(a) of Ref. [20] for a sample of AlN(0001) layer (2 nm) deposited on boron-doped diamond (111) substrate. The two experimental C 1s spectra in Figure 4 shown in bulk-sensitive (θ = 20°) and surface-sensitive (θ = 60°) modes give substantial changes in spectral shapes and peak-positions with change in theta. We can expect that the adventitious C 1s component is dominant in the surface-sensitive mode and the substrate diamond C 1s component increases in the bulk-sensitive mode. The two components are resolved by a curve-fitting procedure as shown in Figure 4 for the bulk-sensitive C 1s spectrum. The result of curve-fitting gives E_{C1s_Dia} = 284.35 eV. If the C 1s spectra were measured at an arbitral theta (let's say θ = 45°), the peak position would be assigned at ~284.8 eV, which marks an error of ~0.45 eV.

3. Diamond heterojunction valence band offset (VBO) studied by XPS in the last decades

Tables 1 and 2 show the summaries of VBO XPS studies for atomic layer deposition (ALD) Al_2O_3 layers on (I) hydrogen-terminated and (II) oxygen-terminated diamond substrates, respectively. Table 3 shows the summaries of VBO XPS studies for thin layers other than ALD Al_2O_3 layers on diamond substrates. We will explain these in this order. The contents in the tables that are not satisfactory in terms of VBO XPS determination are singly underlined. The contents that are related to special procedures are shown in bold characters. Since Tables 1–3 are full in content and self-explanatory, we will describe some important points only. The search for the relevant literature may not be complete so that we may have some missing reports in the Tables.

3.1. VBO XPS studies on ALD Al_2O_3 layers on hydrogen-terminated diamond substrate (Table 1)

Hydrogen-terminated (H-terminated) diamond causes so-called p-type surface conductive layer that is used for field effective transistor (FET) devices and ALD Al_2O_3 layers are used as gate oxides on the channel [32]. Liu et al. [1] were the first to report VBO XPS study on this system. They used a commercial XPS spectrometer with monochromatic Al K_α source. However, essentially no details of XPS measurements were described. For the evaluation of E_{C1s_Dia}-E_{V_Dia} value, an extrapolation point of leading VB edge was used and a wrong value of E_{C1s_Dia}-E_{V_Dia} = 283.1 eV was obtained. The identification of diamond C 1s peak with Al_2O_3 overlayers (4 nm) was not explained but assumed to be the highest peak position, which is most probably that of adventitious C1s of the *ex-situ* XPS sample surface. In addition, the thickness (4 nm) of overlayer may be too large to detect diamond C 1s peak. Thus, VBO value of 2.96 ± 0.2 eV is not reliable. Since E_{C1s_Dia}-E_{V_Dia} = 283.1 eV is smaller by 0.9 eV than the correct value, correct VBO value must be larger by ~0.9 eV at least.

Takahashi et al. [4] reported VBO XPS study on a similar system with NO_2 pre-exposed H-terminated diamond. They used a synchrotron radiation source with $h\nu$ = 700 and 60 eV for core-level and VB, respectively. For the evaluation of E_{C1s_Dia}-E_{V_Dia} value, an onset point of VB spectrum was used to reach with a value of E_{C1s_Dia}-E_{V_Dia} = 284.3 eV, which is a little (~0.3 eV) larger but is close to the correct value. It is to be noted that the onset point of VB spectrum excited by a ultraviolet light is not necessary the VB top [25,33]. The identification of diamond C 1s peak at the junction was made by a depth-profile measurement by Ne^+ sputtering of the sample surface. C 1s peak of a sample after many times of Ne^+ sputtering with a nominal Al_2O_3 thickness of 0.09 nm was assigned to be from diamond at the junction. Smoothness or uniformity of the sample surface was not examined, which is rather risky to be convinced by the above results. Saha et al. [10] reported VBO XPS study on similar systems with NO and SO_2 pre-exposed H-terminated diamond. Method used was the same as that of [4]. The resulting VBO's were essentially same as for NO exposed sample of [4]. Same comments for Takahashi et al. [4] may be made on the results of [10].

Maréchal et al. [7] reported VBO XPS study on ALD Al_2O_3 layers on H-terminated boron-doped p-type (111) diamond and phosphorus-doped n-type(111) diamond.

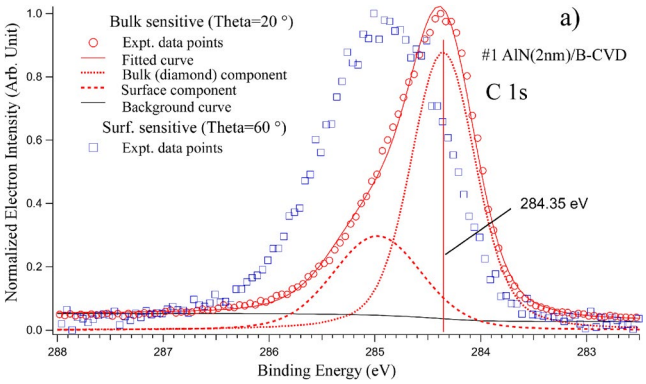


Figure 4. C 1s spectra reproduced from Fig. 6(a) of Ref. [20] for a sample of AlN(0001) layer (2 nm) deposited on boron-doped diamond (111) substrate. (Reprinted with permission from Elsevier under license # 6172371018356.)

Same comments as for [1] can be made for Maréchal et al. [7]. Thus, VBO values of 1.8 ± 0.2 eV on p-type and 2.7 ± 0.2 eV on n-type substrates, respectively, are not reliable.

Yang et al. [9] reported VBO XPS study on plasma-enhanced (PE)-ALD Al_2O_3 layers on H-terminated boron-doped p-type (100) diamond. They used a commercial XPS spectrometer with monochromatic Al K_α source. Notably, the spectrometer was an *in-situ* type and a PE-ALD apparatus was attached to it. For the evaluation of E_{C1s_Dia}-E_{V_Dia} value, VB top position was assigned at zero binding energy position to reach with a value of E_{C1s_Dia}-E_{V_Dia} = 284.1 ± 0.1 eV, which is close to the correct value. The identification of diamond C 1s peak at the junction was assumed to be the highest peak position, which seems to be probable for the *in-site* XPS sample. However, a strange thing about C 1s peak is that the peak position showed a large shift of ~2.0 eV toward larger binding energy side after the first PE-ALD Al_2O_3 deposition then the shifts were restored after H-plasma exposures (cf. Figures 1–3 of Ref. [9]). This shift was ascribed to a band vending shift by the authors, which is not understandable easily. It is more likely that this shift is related to how *in-situ* sample was held in a sample holder of XPS spectrometer. Nothing about sample holding method was described but can be presumed that they used metal (possibly Au-plated metal) clips to press the sample surface. We can expect a Schottky-type barrier happened between ALD Al_2O_3 deposited sample surface and the metal clips which caused so-called photovoltaic effect [24]. When the sample was exposed to H- plasma, the surface was H-terminated and thus Ohmic contact between the metal-clips and sample surface was resumed. This caused the restoring of C1s peak position. Another strange thing about the results of Yang et al. [9] is that C 1s XPS peak intensity did not decay after PE-ALD Al_2O_3 depositions (cf. Figures 1 and 3 of Ref. [9]): As far as the figure captions tell, this must be correct. This indicates that the PE-ALD Al_2O_3 layer may not be a form of layer-by-layer type but in a form of islands. C 1s XPS signal might come from open diamond areas among the Al_2O_3 islands until the open areas were filled by the 20 nm Al_2O_3 layer deposition. It is strongly recommended to have performed a morphological check of the sample surface. For this reason, VBO values of 2.7 eV may not be correct.

Yang et al. [14] extended their previous work [9] to VBO XPS study of MoO_3 layers (2 nm) on PE-ALD Al_2O_3 layers on H-terminated boron-doped p-type (100) diamond. By similar procedures, they obtained VBO values of 2.6 eV for Al_2O_3 layers and VBO values of 3.1 eV for MoO_3 layers on Al_2O_3 layers. The same comments for [9] as above may be applied to this work [14].

In summary of the VBO XPS studies on ALD Al_2O_3 layers on hydrogen-terminated diamond substrate, we would conclude that no rigorous results are obtained.

3.2. VBO XPS studies on ALD Al_2O_3 layers on oxygen-terminated diamond substrate (Table 2)

Oxygen-terminated (O-terminated) diamond causes insulation of surface layers that is used for FET devices to control bulk p-type carriers of lightly B-doped diamond and ALD Al_2O_3 layers are usually used for this purpose. There are three reports of VBO XPS studies on ALD Al_2O_3 layers on oxygen-terminated diamond substrate.

Maréchal et al. [5] reported VBO XPS study on ALD Al_2O_3 layers (2 nm) on O-terminated diamond which was made by vacuum-ultra-violet light/ozone treatment of heavily and lightly B-doped of Ib(100) substrate. For the evaluation of E_{C1s_Dia}-E_{V_Dia} value, an extrapolation point of leading VB edge of O-terminated diamond was used to reach a wrong value of E_{C1s_Dia}-E_{V_Dia} = 282.25 eV. The identification method of diamond C 1s peak with Al_2O_3 overlayers (2 nm) was not explained but assigned to a shoulder at E_B = 284.08 eV (Figure 3(e) of Ref. [5]) to be due to C–Al bond at the interface. This is wrong and strange for the following reasons. If the C 1s component at E_B = 284.08 eV is due to C–Al bond at the interface, there must be the other component of bulk diamond C–C bond, which must be much stronger in intensity, and this C–C bond component must be used for the evaluation of VBO. We could imagine this when we see Figure 3(f) of Ref. [5]: the C–C bond component at E_B = 284.32 eV is much stronger than the

oxygen-contribution components and the intensity ratio of the later component would correspond to that of C–Al bond in Figure 3(e) of Ref. [5]). Since the surface-sensitivity check of Figures 3(e,f) of Ref. [5] was not performed, the location of C–C bond component is not known. Thus, VBO value of 1.43 ± 0.2 eV is not reliable.

Cañas et al. [12] reported VBO XPS study on ALD Al_2O_3 layers on O-terminated diamond which was made by vacuum-ultra-violet light/ozone treatment of lightly B-doped of Ib(100) substrate. For the evaluation of E_{C1s_Dia}-E_{V_Dia} value, an onset point of a substrate diamond VB spectrum was used to reach with a value of E_{C1s_Dia}-E_{V_Dia} = 283.9 eV, which is close to the correct value. The identification of diamond C 1s peak at the junction was made by a depth-profile measurement by Ar^+ sputtering of the sample surface. A VBO value of 3.4 ± 0.2 eV was thus reported. Smoothness or uniformity of the sample surface was not examined, which is rather risky to be convinced by the above results.

Liu et al. [18] reported VBO XPS study on ALD Al_2O_3 layers (3 nm) on O-terminated lightly B-doped diamond with a net-patterned gold (Au) mask. They used a commercial XPS spectrometer with a scanning micro-X-ray source, thus XPS signal from several tens μm spots can be examined. For the evaluation of E_{C1s_Dia}-E_{V_Dia} value, an extrapolation point of leading VB edge of O-terminated diamond without Au mask was used and reached a wrong value of E_{C1s_Dia}-E_{V_Dia} = 283.65 eV. The identification of diamond C 1s peak with Al_2O_3 overlayers was really problematic as explained below.

They compared C 1s XPS spectra (what they call as-received spectra) for the two samples with and without the Au mask (Figure 3(a) of Ref. [18]). They observed a large shift (1.27 eV) of C 1s peaks for the two samples and attributed it to a charge-up effect for the sample with Au mask, which is a strange interpretation. It is not described how the samples were held to a metal sample holder of the XPS spectrometer. If the sample surface and the Au-mask were clamped by a conductive material, the large shift would not happen. It seems that the sample surfaces had no electric connection to the holder and a charge-neutralizer was used. It is known that Au metal on O-terminated diamond forms Schottky-type junction causing the photovoltaic effect during XPS measurements [24]. Since the effect of charge-neutralizer is to make the sample surface potential nearly equal to the vacuum level, the net surface potentials of the two samples with and without Au-mask are about the same. This would make C 1s peak on the open area of Au-masked sample deeper in binding energy due to the presence of Schottky barrier height between Au-mask and O-terminated diamond surface.

Au $4f_{7/2}$ XPS spectra (what they call as-received spectra) of the samples of B-diamond with mask and Al_2O_3 (3 nm)/B-diamond with mask show a peak shift of 0.18 eV (Figure 3(b) of Ref. [18]). This shift certainly shows that the Au-mask was not electrically connected to the holder and further indicates that the charge-neutralizer was used during XPS measurements. They used the as-received Au $4f_{7/2}$ XPS spectra to shift the binding energy scale to obtain what they call calibrated spectra using the ideal binding energy (83.96 eV) of Au $4f_{7/2}$ XPS peak. The resulting C1s and Al 2p spectra are shown as Figure 4(a,c) of Ref. [18]. This calibration strategy has nothing to do with real calibration since we have Schottky junction between Au-mask and O-terminated diamond surface as found in Figure 3(a) of Ref. [18]. This calibration just gives a rigid shift of binding energy scale. In fact, we do not need the Au-mask. What we need is a binding energy difference which is consistent within the same sample. Thus, as-received spectra without the Au-mask will do it. Anyway, they assigned C 1s peak from B-diamond for the sample of Al_2O_3 (3 nm)/B-diamond with mask at E_B = 284.15 eV and assigned another peak at E_B = ~282.5 eV to be due to carbon atoms bonded to dopant B. This cannot be hardly justified. Firstly, C 1s component bonded to dopant B can hardly be detected for the lightly B-doped diamond. If this were the case, we must see it for all the C 1s spectra shown in this literature. Secondly, the most intense C 1s peak at E_B = 284.15 eV for the sample of Al_2O_3 (3 nm)/B-diamond cannot be due to substrate B-diamond. This is because we have 3 nm thick Al_2O_3 overlayers on top of B-diamond and there must be C 1s component due to adventitious carbon-containing molecules adsorbed on the *ex-situ* sample surface. They may argue that the adventitious C 1s component exists at E_B = 284.8 eV for the calibrated spectra. This is not justified either since the calibration has no real meaning. We must perform surface-sensitivity check for the C 1s spectra as in Figure 4a) to find the C 1s component of substrate B-diamond to be sure. Thus, VBO value of 1.30 eV is not reliable.

3.3. VBO XPS studies of second material layers other than ALD Al_2O_3 layers on diamond substrate (Table 3)

Table 3 summarizes VBO XPS studies of second material layers other than ALD Al_2O_3 layers on diamond substrates. For the evaluation of E_{C1s_Dia}-E_{V_Dia} value, extrapolation points of leading VB edge of diamond substrates were used for all the cases to reach wrong values around ~283.0 eV, which is about 1.0 eV smaller than the correct value. Thus, the obtained VBO values are smaller by ~1 eV than correct values at least. The identification method of diamond C 1s peak with the second overlayers was not explained in most cases and assigned to the highest C 1s peaks. The sample holding method and use/nonuse of charge-neutralizer were not specified in all the cases. Further, no surface-sensitivity checks of C 1s spectra were reported. For the reasons mentioned above, VBO values reported in Table 3 are not reliable.

4. Concluding remarks

It is pity to find that most of the researchers working on diamond devices are not aware of the fact that the extrapolation points of leading edge in diamond VB XPS spectra do not coincide with VB top of diamond. It is true that the extrapolation points of leading edge in VB XPS spectra for most materials give its VB top. This must be the reason. We must be aware of the special nature of diamond valence band. It is surprising that most of the researchers working on diamond devices are not aware of the fact that the *ex-situ* samples normally used in XPS measurements are covered with adventitious carbon-containing molecules. This prevents the identification of C 1s XPS peak from the substrate diamond. We must identify the correct peak position by some methodologies such as surface-sensitivity check and ion etching. It is surprising to find that the morphology of sample surfaces is rarely examined. We must be aware that the probing depth of XPS is so small (~ 2 nm) that the sample surface must be uniform in an atomistic scale of ~0.2 nm. This is very important to be checked to be sure about the results of VBO XPS determination.

Disclosure statement

No potential conflict of interest was reported by the author.

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