Determination of transport levels of inorganic semiconductors by ultraviolet and inverse photoemission

S. Krause,[1,2] A. Schöll,[1] and E. Umbach[1,3]

[1]*University of Würzburg, Experimental Physics II, Am Hubland, 97074 Würzburg, Germany*
[2]*Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Bereich Solarenergieforschung,*
Albert-Einstein-Straße 15, 12489 Berlin, Germany
[3]*Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany*

A combination of ultraviolet and inverse photoemission is often used to determine the position of the transport levels of semiconductors. Although data from direct methods like photoemission appear advantageous at first glance, large discrepancies between thus-derived band gaps and optically measured band gaps have led to fundamentally different evaluation methods of the data from ultraviolet photoelectron spectroscopy (UPS)/inverse photoelectron spectroscopy (IPS) experiments, the essential alternatives being the maxima or the onsets of the frontier peaks. In this paper, we review published data as well as present new experimental data for a few representative II-VI and III-V compound and element semiconductors. New data from silicon are utilized as examples for evaluating details of such combined UPS and IPS spectra and for answering the question of how surface effects, especially the consequences of surface reconstruction, can adequately be taken into account. The results clearly indicate that, for all three types of semiconductors, only peak onsets represent the correct band positions. Possible reasons for this finding are discussed, and an explanation in the framework of relaxation (i.e., dynamical screening) is suggested.

I. INTRODUCTION

Fundamental properties of semiconductors are the energy positions of valence and conduction bands with respect to the Fermi level, their difference (transport gap), and the optical gap. Since many new semiconducting or isolating materials have been developed recently or will be developed in the future, simple and reliable (routine) techniques are required to determine the transport levels. The direct methods, ultraviolet photoelectron spectroscopy (UPS) for the occupied valence band and inverse photoelectron spectroscopy (IPS) for the unoccupied conduction band, would be ideally suited for this purpose if the results could unambiguously be interpreted and would be consistent with other data. Because hitherto this did not seem to be the case and because material or semiconductor scientists often do not have direct access to (especially inverse) photoemission equipment, other, nondirect methods were established. Among these are optical absorption, photoconductivity, optical reflection, two-photon photoemission, electron energy loss spectroscopy, photoluminescence, and resonant inelastic x-ray scattering, but these methods usually require special samples, assumptions, or models, the implementation of additional complications (e.g., contacts and their interfaces), the recording and interpretation of characteristic curves, or the combination of indirect results. This may lead to ambiguities and may give rise to large error bars or inconsistencies calling for a consistency check by comparing with independent results from direct techniques. Thus, the question arises whether we can meet the challenge of unambiguously determining transport levels by improving the (evaluation of the) direct methods UPS and IPS.

Ultraviolet photoelectron spectroscopy has been extensively used in the past to determine the energetic structure of occupied levels in various materials. The first time it was used in combination with IPS was in 1984 by Himpsel and Fauster [1]. They investigated silicon without and with silicon-metal alloys on the surface and determined the ferromagnetic exchange splitting energy of cobalt. They—like many others—also utilized this combination of techniques to map occupied and unoccupied bands and to compare the data to theoretical calculations. However, the band gaps were not compared with the values of other methods. A previous paper on this topic was written by Carstensen *et al.* [2] for III-V semiconductors. They noticed that the *distance of the peak maxima* between the valence band maximum (VBM) and conduction band minimum (CBM) is much larger than the optical gap of these materials and claimed that this was due to the fact that UPS and IPS are surface sensitive and that the observed deviation was due to energy level shifts at the surface. Later, they investigated WSe$_2$ and determined a bulk band gap using the peak maxima which was in agreement with optical measurements [3]. This evaluation procedure, however, is not generally accepted.

Other researchers recorded similar data from various systems and determined the CBM and VBM by using the *onsets of the leading peaks*. While this evaluation could be the correct choice if angle-integrated data are being used (hoping that there is enough intensity at VBM/CBM in the spectrum to yield the correct onset) most analyzers are (partially) angle resolving, and many researchers like to control their position in k-space and the influence of density of states (DOS) and matrix element effects by varying the experimental parameters using an angle-resolved spectrometer. The values of the transport gaps derived from the *onsets* generally fit the optical data much better, but no explanation why the onsets instead of the peak maxima were taken was given in the respective literature [4–11]. We note that the large discrepancies of the different evaluation procedures and the missing explanation of why the apparently "better" evaluation method is physically correct have most likely prevented a wider utilization of this apparently simple method.

In this paper, we address the general issue of the determination of the band gap in inorganic semiconductors by using UPS and IPS and also address the understanding of the discrepancies mentioned above. This paper on inorganic semiconductors relates to a previously published paper on the band gap determination of organic semiconductors [12]. In this paper, we compare data from all three types of inorganic semiconductors, II-VI, III-V, and element semiconductors, and utilize already published data if possible, applying a consistent evaluation.

II. EXPERIMENTAL

All measurements were performed in a VG ESCALAB Mk II with a base pressure of better than 2×10^{-10} mbar. The samples, except for silicon, were grown in a Riber 2300 molecular beam epitaxy (MBE) system and then transported in a mobile ultrahigh vacuum (UHV) chamber ($p < 2 \times 10^{-9}$ mbar) to the ESCALAB. The MBE system and the growth of the HgTe and CdTe samples are described elsewhere [13]. The silicon samples were standard Si(001) p-doped wafers flashed in the UHV chamber to 1200 °C for 2 min to remove the native oxide layer. After rapid cooling to 950 °C, the cooling rate was reduced to about 1 °C/s. After this treatment, the samples showed a sharp 2×1 reconstruction with two domains using low energy electron diffraction (LEED).

A gas discharge lamp was employed for UPS, which could be operated either with helium and photon energies of 21.22 and 40.80 eV, respectively, or with argon for 11.62 eV photons. The IPS system consisted of a Ciccacci-type low energy electron gun with a BaO cathode [14] and a Geiger-Müller detector with a SrF$_2$ window filled with Ar and I$_2$ [15]. The detector was used in the isochromatic mode with a fixed photon energy of 9.5 eV. The resolution was 50 meV for UPS and 370 meV for IPS, as determined by a fit of the Fermi edge of a clean Ag(111) sample and a sputter-cleaned gold foil, respectively. The analyzer acceptance angle was set to $\Delta\theta = 2°$ for the $\vec{\text{k}}$-resolved UPS measurements.

III. RESULTS AND DISCUSSION

A. Published UPS and IPS data from various semiconductors

1. II-VI compound semiconductors

The data displayed in Fig. 1 have been published in Ref. [13] and show the combined UPS and IPS spectra of the two II-VI semiconductors CdTe [Fig. 1(a)] and HgTe [Fig. 1(b)]. The surface of both samples was $c(2 \times 2)$ reconstructed and did not show any surface states near the VBM or near the CBM. This absence of surface states between VBM and Fermi energy can be seen in Ref. [13] by comparing spectra recorded with He I and Ar I excitation energy. The fact that a shift of the leading edge is found identifies the structures in this energy region as bulk states since surface states do not show any vertical dispersion. Indeed, the selected photon energy (Ar I) and emission angle result in data from the Γ point.

It is important to note that both datasets were recorded k-resolved and taken close to the center of the Brillouin zone (BZ), thus representing the energy region of the direct band gap. Data from other regions of the BZ yield of course larger
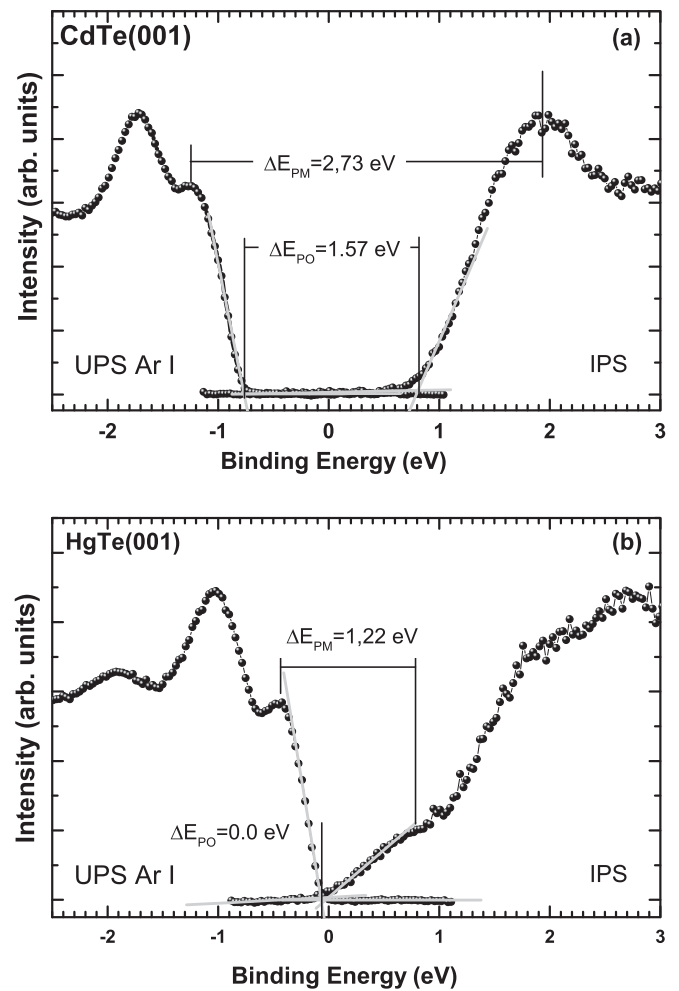

FIG. 1. Combined UPS ($h\nu = 11.62$ eV, Ar I) and IPS spectra of CdTe(001) and HgTe(001) (from Ref. [13]). The data were recorded with normal emission of the photoelectrons and normal incidence of the electron beam, respectively. Both samples showed $c(2 \times 2)$ reconstructed surfaces but no surface states. The gray lines illustrate the determination of the peak onsets; the separations of peak maxima and peak onsets are indicated.

differences of the band offsets according to the band structure situation in the respective part of k-space and hence would not be comparable to the optical absorption data.

In each part of Fig. 1, two sets of lines illustrate the different possibilities to obtain the values for the VBM and the CBM. ΔE_{PM} and ΔE_{PO} represent the separation of the peak maxima and the peak onsets, respectively. Of course, one may ask whether the peak maxima indeed represent VBM and CBM or whether matrix element effects suppress the respective signals. In the present case, this can be excluded after careful experiments (variation of photon energy and emission angle) and comparison with calculations, but in general, this could be a problem that (additionally) obscures the use of peak maxima (an example is the IPS spectrum of HgSe where the CBM peak has nearly no intensity; not shown). While a determination of peak maxima is easily possible in many cases, the determination of onsets is often less obvious because limited energy resolution (e.g., for IPS), features near the band gap (e.g., surface states, impurities), or a structured

background covers the energy region of interest. The onset is usually derived by taking the intersection of lines fitted to the rising tails of the frontier peaks and a background line (these are indicated in Fig. 1 by gray lines).

In Fig. 1, this evaluation yields values of $\Delta E_{PM} = 2.73$ eV and $\Delta E_{PO} = 1.57$ eV, respectively, for CdTe(001) [Fig. 1(a)] as well as $\Delta E_{PM} = 1.22$ eV and $\Delta E_{PO} = 0$ eV for HgTe(001) [Fig. 1(b)]. The band gap values derived from optical absorption measurements ($E_{g,opt}$ in the following) are 1.57 eV for CdTe and 0.00 eV for HgTe [13] (because HgTe is a semimetal). The optical band gaps fit perfectly to the ΔE_{PO} values from the UPS/IPS spectra, whereas the values for ΔE_{PM} deviate by more than 1 eV. A difference between the optical band gap (as measured by optical absorption) and the transport band gap (as intended to be measured by UPS/IPS) could arise because of the binding energy between excited electron and created hole if these form an electron-hole pair (exciton). However, since for these semiconductors the exciton binding energies are relatively small (a few millielectronvolts to about 100 meV [16]), they are not relevant for the comparison between the optical data and the data for the transport gap, at least not within the error bar of the UPS (± 0.1 eV)/IPS results (± 0.2 eV). Thus, we can clearly state that the ΔE_{PM} values are by far not compatible with the optical data, while the ΔE_{PO} data are in excellent agreement.

2. III-V compound semiconductors

Since the paper by Carstensen *et al.* [2] provides UPS/IPS experimental data for several III-V semiconductors, we did not perform our own experiments. Again, the ΔE_{PM} values given by Carstensen *et al.* do not match the band gap values from optical absorption (see Table I) as shown above for the II-VI compounds and also observed for other classes of materials. We note that the data were taken from samples cleaved in UHV in (110) direction and were collected without any further treatment at several points of the surface BZ (SBZ) using He I radiation (21.22 eV). The authors claimed that they evaluated "surface band gaps" by determining the maxima of the peaks closest to the Fermi level at the Γ point of the SBZ. Neither have bulk contributions to the spectrum been considered, nor have possible surface states been identified. The thus-determined differences to the optical data $\Delta E_{PM} - E_{g,opt}$

range from 0.7 to 1.3 eV; they are attributed to the difference of bulk band gaps (as determined by optical adsorption) and surface band gaps (as determined by UPS/IPS).

In order to compare with our present approach, we have reevaluated the III-V data of Ref. [2] using the onsets of the UPS and IPS spectra. The resulting ΔE_{PO} data are also given in Table I and fit much better to the optical data. We note, however, that the error bars are larger (see table caption) than for our own data of Fig. 1 due to the uncertainties of this indirect evaluation procedure. The question whether only surface states—or also only bulk states—are seen in the photoemission data and how much the onsets represent the bulk band properties will be addressed below.

3. Element semiconductors

The situation is more complicated for element semiconductors due to the strong contributions from surface states arising from surface reconstructions. Table I also contains a value for germanium yielding a difference between E_{PM} and $E_{g,opt}$ of 1.1 eV. This UPS data from Kipp *et al.* [17] was gained from a carefully prepared Ge(001) (2 × 1) crystal using variable photon energies. The surface band gap in this case was determined as energetic difference of the maxima of the peaks attributed to surface states, averaged over all high symmetry points of the SBZ. Since the surface states play an important role and since the energy resolution of the IPS data of Ref. [17] appears rather low, we have recorded our own data but have taken Si (001) instead of Ge for practical reasons. These results will be discussed in the next section.

B. Band gap determination of silicon

In order to consider the influence of the prominent surface states in element semiconductors in more detail, we have investigated as an example a (2 × 1) reconstructed Si(001) sample. The corresponding UPS and IPS spectra are displayed in Fig. 2 together with an evaluation of ΔE_{PM} and ΔE_{PO} as discussed above. The resulting values are $\Delta E_{PM} = 2.2$ eV and $\Delta E_{PO} = 1.1$ eV, respectively, the latter value being again in excellent agreement with the optical data. However, due to the existence of very pronounced surface states, the evaluation is by far not as straightforward as in

TABLE I. Surface band gaps determined from the data of Figs. 1–3 together with data and optical gaps from Refs. [2,13,17,27]. The error is estimated to about ± 50 meV in the case of our UPS and about ± 100 meV in the case of our IPS data. For the III-V semiconductors, the peak maxima data are taken from the original paper, but the evaluation of the onsets (not given in the references) was done in the context of this paper. The accuracy of such a reevaluation is of course limited (0.2–0.4 eV, depending on the specific case).

| Semiconductor	Peak maxima ΔE_{PM} (eV)	Peak onsets ΔE_{PO} (eV)	Optical gap ΔE_{OG} (eV)
GaP	3.0 [2]	2.2 [evaluated this paper]	2.26 [2]
GaAs	2.4 [2]	1.4 [evaluated this paper]	1.42 [2]
GaSb	1.9 [2]	0.4 [evaluated this paper]	0.72 [2]
InP	2.4 [2]	1.3 [evaluated this paper]	1.35 [2]
InAs	1.7 [2]	0.7 [evaluated this paper]	0.36 [2]
InSb	1.4 [2]	0.3 [evaluated this paper]	0.17 [2]
Ge	1.9 [17]		1.1 [17]
CdTe(001)	2.73 [13]	1.57 [13]	1.57 [13]
HgTe(001)	1.22 [13]	0 [13]	0 [13]
Si(001) (2 × 1)	2.15 [this paper]	1.1 [this paper]	1.12 [27]
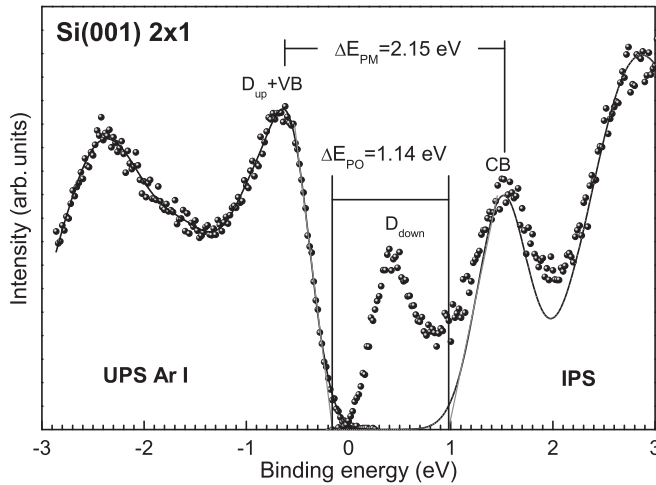
FIG. 2. Combined UPS ($h\nu = 11.62$ eV, Ar I, normal emission) and IPS spectra (normal incidence) for the (2×1) reconstructed Si(001) surface. Solid lines represent the result of a curve fit, where in the IPS data the surface state D_{down} has been subtracted, and the resulting spectrum was deconvoluted by a Gaussian function of 370 meV width. The gray lines illustrate the determination of the peak onsets.

the II-VI semiconductor case. Various aspects have to be considered before a (sufficiently reliable) assignment of peaks or onsets, and hence of the band gap, can be derived from the photoelectron spectroscopy data. The following discussion is hence an example of which measures may have to be taken for a direct determination of the transport gap in this case.

1. Position in the 3D BZ

For the interpretation of the data including the correct assignment of the bulk electronic structure, it is necessary to know the position within the 3D BZ to which the respective data belongs and to vary the parameters of the experiment such that the band structure close to the extrema is revealed. Only if data is available representing the CBM and the VBM, a correct band gap can be determined. Modern electron analyzers in combination with monochromatized light sources allow one to study the electronic structure in more detail and to compare the experimental band structure to a calculation [19].

The combined UPS-IPS spectra of a (2×1) reconstructed Si(001) sample are displayed in Fig. 2. The IPS spectrum (see also Fig. 3) was recorded in normal incidence where $\vec{k}$ ends at 0.15–0.00 of $\overline{\Gamma X}$ (depending on the binding energy). The state at 1.50 eV has been identified as a transition from the high lying Δ_{1c} band down to the X_{1c} point by Ortega and Himpsel [20]. This means that a bulk reciprocal vector $\vec{G}_{111}$ is involved and that this state lies close to the CBM. The states at 2.89 and 4.15 eV are bulk states close to Γ_{15c} and $\Gamma_{2'c}$. It is possible that additional transitions contribute to the spectrum since the three peaks, which are identified as bulk states, have significantly different widths. A complete assignment (which is irrelevant in the present context) is only possible with the help of appropriate calculations. A very recent (critical) discussion can be found in Ref. [19].
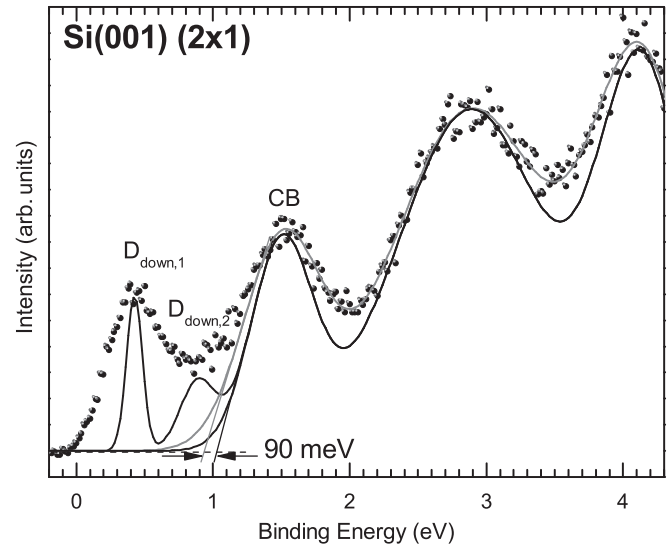

FIG. 3. IPS spectrum of the Si(001) (2×1) surface (dots) together with a deconvoluted curve fit (black line). The two surface state components ($D_{\text{down},1}$ and $D_{\text{down},2}$) are well distinguished due to their small line width resulting in a marked narrowing after deconvolution. In addition, the deconvoluted spectrum after subtraction of the surface states is compared to the fit to the data before deconvolution (gray line) in order to visualize the shift of the onsets due to experimental resolution.

The UPS data was measured with Ar I (11.62 eV) in normal emission representing a point in k-space about halfway between Γ and X [21]. The first peak has three components of which the one with the lowest binding energy originates from a bulk state close to the $\Gamma_{25'v}$ point. The other two components are surface states. An assignment of the transitions referring to the UPS peaks can be found in Ref. [18].

2. Surface states

It is important to note that the VBM and the CBM are usually not easy to identify since they can be superimposed by surface states, which in the case of Si have their origin in so-called dangling bonds. These reactive, unsaturated orbitals at the surface usually either recombine with each other, leading to the formation of a surface reconstruction, or they bind to residual gases such as oxygen or hydrogen. The surface states of semiconductor surfaces were intensively investigated with photoelectron spectroscopy in the late 1980s and 1990s (see e.g. Ref. [18]). Also, other types of gap states are possible such as the ones produced by excessive doping and impurities, which lead to new states slightly below the CBM and above the VBM. Usually these dopants and impurities have very low concentration and cannot be sensed with PES. An elaborate review about semiconductor surface states was published by Hansson and Uhrberg in 1988 [18].

For the Si(001) (2×1) surface, there are well-known surface states which originate from the asymmetric silicon dimers at the surface. The silicon atom closer to the surface has an additional occupied orbital (D_{up}), the one farther away an unoccupied orbital (D_{down}). Since our crystal did not have a 4° miscut towards the (011) plane, which can be used to generate a single reconstruction domain, we have to deal

with additional components to the D_{down} and D_{up} states as shown in [18]. This could be verified by LEED, which showed spots from a second surface domain. In the IPS spectrum, these surface states appear in the band gap and have binding energies of 0.43 and 0.88 eV above the Fermi level. Similar surface states with such binding energies have been observed by Johansson and Reihl [22] for single domain Si(001) (2 × 1). Recent two photon photoemission measurements on single domain Si(001) 2 × 1 by Weinelt *et al.* [23] resulted in a D_{down} signal at 0.65 eV and another surface feature (labeled *X* in their paper) at 0.52 eV. The occupied counterparts of these states appear close to the Fermi energy in the UPS spectrum.

In practice, there are two ways to get rid of the surface states. An experimental approach would be to saturate the surface with, for example, hydrogen [24] or sulfur [25] and hope that any new signals from the adsorbates are far enough from the VBM and CBM. Johansson *et al.* [26] and Hansson and Uhrberg [18] have removed the surface states related to the silicon dimers by hydrogen termination. The interaction with hydrogen will produce a new state at 4.7 eV below E_F in the maximum of the valence band, but no other states near the VBM. This method was also successfully applied in this paper. The removal of surface states was not applicable in the case of the IPS spectrum since it also deletes the umklapp process (which allows the measurement of the CBM) and hence the desired information from the CBM; it was not possible to reach this point in the BZ by variation of the angle of the incident beam.

Another possibility to deal with surface states would be to identify and eliminate the contributions from surface states by fitting the experimental curves accordingly. This can be facilitated by the choice of an appropriate excitation energy (for UPS Ar I, as utilized for recording the data of Fig. 2), which helps to reduce the influence of the surface and brings us as close as possible to the Γ point of the bulk BZ. For IPS, the result of this approach is shown in Fig. 3, where the gray lines refer to the fitted curves. Five Gaussian peaks with adjustable width describe the data very well. Two of them refer to the D_{down} state and were subsequently removed. The solid line used for the onset determination is the result of an additional deconvolution in order to get rid of the detector broadening (which is discussed in the next section).

On the UPS side, the split D_{up} surface states could not be unambiguously identified, and thus their contributions could not be eliminated by curve fitting. However, there are good reasons [18,22] to believe that the onset of the combined peak has at least a large contribution from the bulk and thus can be used to determine ΔE_{PO}. Such reasons are the expected intensity and energy position of the bulk state and their dependence on photon energy. Another reason is that a value of $\Delta E_{PO} = 1.1$ eV is thus derived, which is within the error bar identical with the value $E_{g,opt} = 1.12$ eV for this indirect band gap obtained from optical absorption [27,28].

C. Relevant aspects for the determination of band edges from PES spectra

In this section, we will address aspects that are important for the interpretation of UPS/IPS spectra with respect to the direct determination of the transport gap and the decision whether peak maxima or onsets should be taken for this purpose. The arguments are meant as contribution to resolve the conflicting results and interpretations found in the literature.

1. Surface properties

It is well known that the electronic structure of the surface including the band gap can be quite different from that of the bulk. This arises because of the missing neighbors on the vacuum side which lead to a rearrangement of the surface atoms and even to the formation of new bonds resulting in surface reconstructions and readjusted (dipole) fields at the surface such that the surface free energy is minimized. This rearrangement results in surface bands which either lie in band gaps of the bulk (surface states) or couple to bulk states (surface resonances). Surface reconstructions and the formation of surface electronic states occur in nearly all solids but appear to be the more pronounced the more covalent the character of the interatomic bonding is. Thus, the discrimination of surface with respect to bulk effects is always an issue if surface sensitive analysis techniques are being utilized. Of course it is an issue in the present case for the determination of transport (band) gaps, in particular for the element semiconductors.

2. Surface sensitivity

The question, however, is how much the surface contributes to the electron spectra. Electron energies in UPS/IPS with lab sources are in the range of 5–50 eV (with respect to the Fermi level) and thus refer to an inelastic mean free path (IMPF) of 5 to 0.5 nm (see, for example, Ref. [29]). Thus, a UPS/IPS spectrum has of course a considerable contribution from the first layer. However, this also means that a significant part of the spectral information stems from deeper layers, even in the case of maximum surface sensitivity. Figure 4 shows the percentage of the first layer of the total spectrum in the range from 5 to 50 eV, as calculated for silicon using the standard attenuation formulae [29] as rough
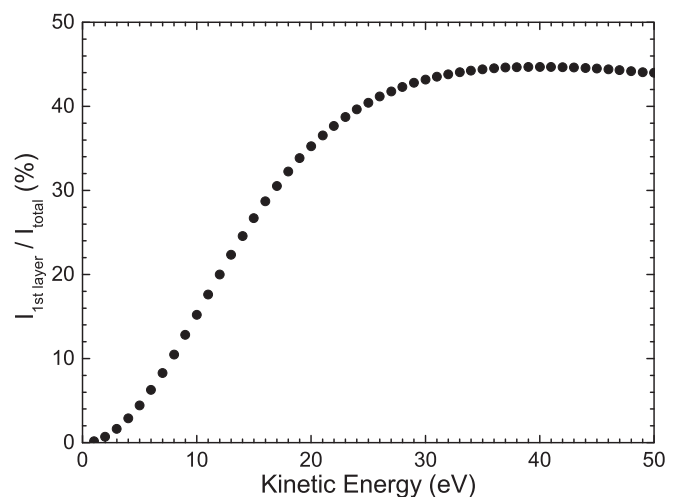

FIG. 4. Calculated values for the contribution of the first layer ($I_{\text{1st layer}}$) of Si to the total photoemission intensity (I_{total}) are shown as a function of kinetic energy (with respect to E_{Fermi}). They are plotted from 1 to 50 eV and calculated with the formula from Seah and Dench (Ref. [29]) for inorganic solids. The monolayer thickness of 0.2715 nm is half the lattice constant.

approximation. This first layer contribution has a maximum of 45% at about 40 eV. At ∼20 eV (He I) and at ∼10 eV (Ar I), the first layer contributes 35% and 15%, respectively, which is consistent with literature [30]. From the available data, we therefore conclude that, in the published spectra of III-V semiconductors [2], the bulk contributions dominate and that our evaluation of using the onsets leads also in this case to the determination of the transport gap.

3. Band bending

Another surface effect that should be briefly mentioned is band bending. This occurs if surface states in the gap are (partially) filled with charge such that an electric field perpendicular to the surface arises, leading to a change of the surface potential and hence to a bending of the bands. Since band bending usually extends over several hundred nanometers, photoemission techniques measure the band positions at the surface rather than in the bulk, but since the bending is equal for all bands, it does not play any role in the determination of the transport band gap and hence can be neglected in the present context.

4. Experimental energy resolution

The experimental resolution is very important for distinguishing peaks (states) or for learning more from the line shapes, but has little influence on the determination of peak energies (in the case of well-separated peaks). However, it has a small influence on the determination of onsets. The experimental resolution of UPS is about 10 times higher than that of IPS where one may take it into account when the onset is being evaluated.

It is interesting in the present case that the observed peak widths in UPS and IPS do not differ substantially, thus indicating a dominating influence of other effects on the line shape. One effect can be derived by deconvoluting the IPS spectra with an experimental broadening of 370 meV (as demonstrated in Fig. 3 for Si(001) 2×1), which leads only to minor changes in the line shape for the bulk signals. The surface states, however, undergo drastic changes due to their smaller line width because of a much smaller lifetime broadening of 2D surface states [31]. After deconvolution, one notices a shift of the onset of the peak assigned to the CBM of about 90 meV in the present case. This gives the size of the (negligible) correction of the onset determination in the case of experimental broadening in IPS.

5. Angular resolution

The angular resolution of the spectrometer plays a major role for the resolution in k-space and hence also for the determination of band positions. Depending on the location in k-space and on the size of the band dispersion, this effect may lead to an inaccuracy of a few tenths of an electronvolt for an angle-resolving analyzer. Only for measurements in k-space close to the band extrema (VBM or CBM) is this effect smaller than the error bar from other sources (i.e. <0.1 eV) and is then negligible.

For the determination of band extrema by using the peak onsets, the angular resolution hardly plays a role as long as the signal from the extrema is contained in the spectra, i.e., as long as the corresponding part of k-space lies within the

acceptance angle of the analyzer. Thus, for the determination of the transport gap by using peak onsets, it might be easier to use a partially angle-integrating analyzer because then an accurate positioning in k-space is less important. In other words, the onsets remain constant for small variations of k around the optimum position. However, then it has to be confirmed that the emission from VBM or CBM contributes sufficiently to the spectrum and is not suppressed due to matrix element effects.

The situation is slightly different when using an electron analyzer that simultaneously measures the spectrum k-resolved. In such cases, it is possible to measure the full $k_\parallel$-cone in a single experiment and thus to obtain the full band structure [32,33]. In order to then accurately determine the position of the band edges, it is then necessary to integrate over some $k_\parallel$-space and to reduce the data to a 1D spectrum. In the 2D or 3D representation, the visible band edges very much depend on the visualization parameters.

6. Relaxation effects

The binding energy measured by photoemission strongly depends on relaxation, i.e., dynamical screening effects. If a hole is created in a solid by a photoionization process, the multielectron systems react by a rearrangement of charge in order to minimize the total energy. If this relaxation process happens on the same timescale the photoionization process (i.e., quasi-instantaneously), the emitted electron carries this information, i.e. its kinetic energy corresponds to the binding energy of the relaxed system. The question thus is how fast and how complete the (positive) charge is distributed within the solid. For instance, for an s electron at the Fermi edge of a metal, the relaxation process is instantaneous and complete, i.e., the photohole is completely delocalized within the solid; thus, the screening is perfect, the binding energy (at the Fermi edge) is zero. For a localized orbital, however, the positive charge may essentially remain localized during the photoemission process—apart from some rearrangement of electrons "around" the hole—such that the emitted electron has a lower kinetic energy as compared to a fully relaxed final state. Thus, photoemission measures an excited (photoionized) state rather than the electronic state of a fully relaxed system. This happens, for example, in the case of core electrons or of f electrons in rare earth metals and can give rise to differences of several electronvolts between excited and fully relaxed final state.

For the determination of transport band positions, however, we need the energy of the fully relaxed state. Therefore, the question is which electronic state we measure if we determine the extremal points of a semiconductor band structure by photoemission. If we take peak maxima, we implicitly assume that the measured electronic states represent the fully relaxed state. However, it is unclear whether this is in fact the case. The observation that band gaps derived from peak maxima are too large by more than an electronvolt and that this deviation differs between different semiconductors gives rise to the interpretation that there is a considerable influence of incomplete relaxation. This interpretation is corroborated by the relatively large peak widths which are similar for all bulk states and much larger than the experimental peak widths (at least in UPS). These are attributed to lifetime broadening that appears to be present in all bulk valence states of semiconductors and amounts to several tenths of an

electronvolt (in contrast to surface states which have widths <0.1 eV or to topological insulator states with widths of a few tens of millielectronvolts [32]). Such a lifetime broadening is consistent with the assumption that the relaxation or dynamic screening process occurs on the timescale of the photoemission process or, in other words, that the measured peak positions do not represent the completely relaxed final state that we need for the determination of band positions. A rough estimate based on adsorbate systems with varying bonding strengths and hence different charge delocalization (relaxation) times gives 1 eV as the order of magnitude for this effect for strongly coupled (semiconductorlike) systems [34]. We thus conclude that the question whether photoemission measures the ionic ground state (i.e., the fully relaxed hole state) and hence the band position responsible for the transport gap is critical because the effect may be in the order of an electronvolt.

IV. CONCLUDING DISCUSSION

The combination of UPS and IPS can successfully be used to determine the transport gap. In many cases, authors employed the peak onsets (without explanation) for obtaining the correct values of the VBM and CBM. However, the lack of a plausible explanation why the peak maxima do not give the right band gaps although they are widely used for determining band positions may prevent other potential researchers from using this method. Also, this paper uses peak onsets (instead of peak maxima), yielding very good agreement between values derived from (direct and inverse) photoemission and those from optical measurements for representative inorganic semiconductors, i.e., II-VI, III-V, and element semiconductors (for organic semiconductors, this has been shown in a previous publication [12]). We note, however, that one has to make sure that the data are taken in the correct part of the BZ by choosing a suited combination of photon (electron) energy and emission (incidence) angle. We further note that surface states have to be properly taken into account (or suppressed) which is particularly important for strongly reconstructed surfaces as in the case of element semiconductors. Other influences (band bending, surface sensitivity, angular and energy resolution) are of no or minor importance.

The only remaining question is why the peak onsets and not the peak maxima give the right values for the transport gap. Our interpretation is directly related to the question whether photoemission measures the completely relaxed (i.e., fully screened) final state which would be the state relevant for the energy position of the transport level. The (experimental) answer is apparently no: On the timescale of the photoemission process, the photohole (or injected electron) is with a certain probability localized, i.e., the charge is not yet completely distributed within the solid before the photoemission process is finished. In such a scenario, we would have two extreme cases: charge completely localized and charge completely delocalized; and the actual measurement would yield a probability distribution between these two cases as schematically shown for the photoemission case in Fig. 5. Note that this curve does not represent a peak with lifetime broadening but is a probability distribution of final states ("peaks") with different screening. Such a distribution is actually represented by a spectral function that describes the dynamic screening
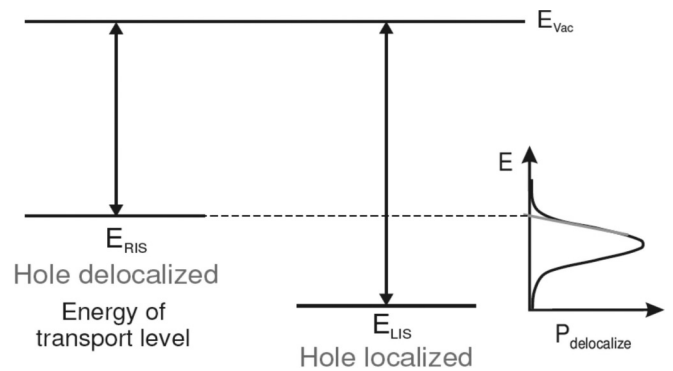

FIG. 5. Schematic illustration of the influence of dynamic charge delocalization on peak shape and position. On the left side, the energy position of fully relaxed (i.e., fully screened) ionic state and, in the middle, the fully localized ionic state are depicted. On the right side, a schematic probability distribution reflects the dynamics of charge delocalization. The onset of this distribution (which is actually a spectral function describing the dynamic screening) may be measured as a relatively broad peak in the photoemission spectrum, thus yielding the position of the VBM.

and has, for example, been derived by Schönhammer and Gunnarsson [35], Gunnarsson and Schönhammer [36], and Fuggle *et al.* [37] in the framework of a modified Andersson model for core level photoemission from weakly coupled chemisorbates and f-metals [38]. Chemisorbates are well-suited model systems to study dynamic screening because their bonding strength [e.g., of CO, N_2, 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA)] to the substrate can be "tuned" by the selection of the substrate, thus spanning the whole range from metallic to insulating behavior [34]. In fact, the Schönhammer-Gunnarsson model describes the strongly varying spectra of, for example, CO on various metals [34,37] qualitatively very well, proving that these spectra are dominated by screening effects that lead to a peak distribution over several electronvolts.

Such an interpretation would explain why we have to take the peak onsets since these approximately represent the extreme (fully relaxed) case relevant for the transport level. It would also explain why the peaks are much broader than the experimental resolution and the band widths (within the recorded part of the BZ). Moreover, it would explain why absolute values of measured band positions (using PES data evaluating peak maxima) sometimes do not agree with calculations or other measurements, in particular if localized states are addressed.

Independent of the validity of this interpretation, the main message of this paper is that the use of peak onsets gives the correct values of band extrema and hence the correct transport gap.

[1] F. J. Himpsel and T. Fauster, J. Vac. Sci. Technol. A **2**, 815 (1984).

[2] H. Carstensen, R. Claessen, R. Manzke, and M. Skibowski, Phys. Rev. B **41**, 9880 (1990).

[3] M. Traving, M. Boehme, L. Kipp, M. Skibowski, F. Starrost, E. E. Krasovskii, A. Perlov, and W. Schattke, Phys. Rev. B **55**, 10392 (1997).

[4] K. M. Tracy, W. J. Mecouch, R. F. Davis, and R. J. Nemanich, J. Appl. Phys. **94**, 3163 (2003).

[5] L. Diederich, O. Kuttel, P. Aebi, and L. Schlapbach, Surf. Sci. **418**, 219 (1998).

[6] V. A. Gritsenko, A. V. Shaposhnikov, W. M. Kwok, H. Wong, and G. M. Jidomirov, Thin Solid Films **437**, 135 (2003).

[7] M. T. Cuberes, A. Bauer, H. J. Wen, M. Prietsch, and G. Kaindl, J. Vac. Sci. Technol. B **12**, 2646 (1994).

[8] Y. Ueda, A. Furuta, H. Okuda, M. Nakatake, H. Sato, H. Namatame, and M. Taniguchi, J. Electron Spectrosc. Relat. Phenom. **101**, 677 (1999).

[9] T. D. Kelly, J. C. Petrosky, D. Turner, J. W. McClory, J. M. Mann, J. W. Kolis, X. Zhang, and P. A. Dowben, Phys. Status Solidi RRL **8**, 283 (2014).

[10] M. Bär, S. Nishiwaki, L. Weinhardt, S. Pookpanratana, O. Fuchs, M. Blum, W. Yang, J. D. Denlinger, W. N. Shafarman, and C. Heske, Appl. Phys. Lett. **93**, 244103 (2008).

[11] E. Bersch, S. Rangan, R. A. Bartynski, E. Garfunkel, and E. Vescovo, Phys. Rev. B **78**, 085114 (2008).

[12] S. Krause, M. B. Casu, A. Schöll, and E. Umbach, New J. Phys. **10**, 085001 (2008).

[13] D. Eich, K. Ortner, U. Groh, Z. H. Chen, C. R. Becker, G. Landwehr, R. Fink, and E. Umbach, Phys. Status Solidi A **173**, 261 (1999).

[14] F. Ciccacci, E. Vescovo, S. Derossi, and M. Tosca, Nucl. Instrum. Meth. B **53**, 218 (1991).

[15] V. Dose, Appl. Phys. **14**, 117 (1977).

[16] M. Dvorak, S.-H. Wei, and Z. Wu, Phys. Rev. Lett. **110**, 016402 (2013).

[17] L. Kipp, R. Manzke, and M. Skibowski, Surf. Sci. **270**, 854 (1992).

[18] G. V. Hansson and R. I. G. Uhrberg, Surf. Sci. Rep. **9**, 197 (1988).

[19] H. Seo, R. C. Hatch, P. Ponath, M. Choi, A. B. Posadas, and A. A. Demkov, Phys. Rev. B **89**, 115318 (2014).

[20] J. E. Ortega and F. J. Himpsel, Phys. Rev. B **47**, 2130 (1993).

[21] L. S. O. Johansson, P. E. S. Persson, U. O. Karlsson, and R. I. G. Uhrberg, Phys. Rev. B **42**, 8991 (1990).

[22] L. S. O. Johansson and B. Reihl, Surf. Sci. **269–270**, 810 (1992).

[23] M. Weinelt, M. Kutschera, R. Schmidt, C. Orth, T. Fauster, and M. Rohlfing, Appl. Phys. A **80**, 995 (2005).

[24] J. W. Cho and R. J. Nemanich, Phys. Rev. B **46**, 15212 (1992).

[25] Y. Fukuda, S. Ichikawa, M. Shimomura, N. Sanada, and Y. Suzuki, Vacuum **67**, 37 (2002).

[26] L. S. O. Johansson, R. I. G. Uhrberg, and G. V. Hansson, Phys. Rev. B **38**, 13490 (1988).

[27] G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).

[28] W. C. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).

[29] M. P. Seah and W. A. Dench, Surf. Interface Anal. **1**, 2 (1979).

[30] S. Hüfner, *Photoelectron Spectroscopy* (Springer, Berlin, Heidelberg, 1995).

[31] J. Kliewer, R. Berndt, E. V. Chulkov, V. M. Silkin, P. M. Echenique, and S. Crampin, Science **288**, 1399 (2000).

[32] R. Ovsyannikov, P. Karlsson, M. Lundqvist, C. Lupulescu, W. Eberhardt, A. Föhlisch, S. Svensson, and N. Mårtensson, J. Electron Spectrosc. Relat. Phenom. **191**, 92 (2013).

[33] A. Vollmer, R. Ovsyannikov, M. Gorgoi, S. Krause, M. Oehzelt, A. Lindblad, N. Mårtensson, S. Svensson, P. Karlsson, M. Lundvuist, T. Schmeiler, J. Pflaum, and N. Koch, J. Electron Spectrosc. Relat. Phenom. **185**, 55 (2012).

[34] W. Wurth, D. Coulman, A. Puschmann, D. Menzel, and E. Umbach, Phys. Rev. B **41**, 12933 (1990).

[35] K. Schönhammer and O. Gunnarsson, Solid State Commun. **23**, 691 (1977).

[36] O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. **41**, 1608 (1978).

[37] J. C. Fuggle, E. Umbach, D. Menzel, K. Wandelt, and C. R. Brundle, Solid State Commun. **27**, 65 (1978).

[38] O. Gunnarsson and K. Schönhammer, Phys. Scr. **T19A**, 273 (1987).