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Influence of As passivation on the electronic level alignment at BeTe/Si(111) interfaces

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We have investigated the influence of As substrate passivation on the electronic level alignment of the heterovalent BeTe/Si(111) interface. Employing photoelectron spectroscopy, we have performed *k*-resolved measurements at selected excitation energies in the uv range to maximize the contribution from the Γ point for a correct determination of the valence band maximum. These results are compared with *k*-integrated data using a density-of-states function from density functional theory. For BeTe(100) and BeTe(111), we find a negligible influence of surface orientation on the position of the valence band maximum. The As passivation increases the valence band offset by 0.24 eV (±0.13 eV) compared to BeTe on an unpassivated Si substrate, thus leading to a significantly increased step in the valence band (0.37±0.13 eV). The results are discussed with respect to the barriers for electron and hole injection in heterostructures and with respect to the interface structure.

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I. INTRODUCTION

Among the II-VI semiconductors, BeTe shows a wide range of interesting physical and electronic properties. First, with its high indirect band gap of 2.8 eV,[1] this material is a promising candidate for double-barrier resonant-tunneling diodes.[2] Second, due to a high covalent fraction of the chemical bond, BeTe exhibits a low stacking fault density, which, especially in heteroepitaxial growth, can lead to layers of high crystalline quality.[2] This suggests the use of BeTe as an interlayer in heterovalent interfaces to improve the crystal quality of successively deposited II-VI layers.[3,4] Third, in the innovative field of spintronics, $Be_{1-x}Mn_xTe$ compounds ($x\sim 0.1$) have recently proved to be suitable materials for spin-manipulating devices.[5]

An important issue in the application of II-VI-semiconductor films is the availability of high quality substrate materials. Very often a connection to established technologies (e.g., silicon) is desired to integrate the corresponding electronic circuit on the same chip and to profit from lower costs and easier and well-established handling. Although not allowing an active spin manipulation, Si is also advantageous in the context of spintronic devices. The extremely long spin relaxation time of up to 30 μs results in a mean free path of spin-polarized electrons up to 3 m,[6] and hence Si is ideally suited for the transport of spin-polarized carriers within a spintronic device.

In our study, we present an investigation of the BeTe/Si(111) interface. This material combination serves as a starting point and model system for Mn-containing compounds. Using Si substrates in (111) orientation has the advantage of avoiding double domains due to symmetry reasons. Also, in many applications, a (111) orientation of the overlayer is desired (e.g., in $Hg_{1-x}Cd_xTe$-based infrared detectors).[4,7]

When using heterovalent interfaces a number of issues have to be resolved. For example, the unbalanced number of valence electrons at the interface can lead to intermixing processes[8,9] and/or to a reduced crystal quality.[9] Such intermixing processes are influenced by the details of substrate preparation and growth conditions[8] as well as by incorporation of different atoms, e.g., in growth start pretreatments,[9,10] and can lead to substantial variations in valence and conduction band discontinuities between substrate and overlayer.[8] Therefore, it is important to investigate the band offsets for each material system experimentally and in detail, because the offsets play a crucial role in the charge transport across the interface.

Taking all these considerations into account, this study employs photoelectron spectroscopy (PES) to investigate the electronic and chemical interface properties of BeTe/Si(111) and the influence of As passivation of the substrate. Furthermore, this paper addresses some fundamental aspects of the accurate determination of valence band offsets by PES.

II. EXPERIMENT

A vast variety of methods to prepare Si samples for molecular beam epitaxy (MBE) have been developed. In our investigation, we focus on the As passivation of the Si(111) surface generated by an exposure to an As beam in ultrahigh vacuum (UHV). We compare our results with those obtained for an unpassivated surface prepared by a chemical H-passivation procedure and subsequent H desorption. To refer to the latter preparation, we will use the notation ''Si-(H).''

All samples were cleaned by an RCA etch,[11] which is a modified version of the Shiraki etch.[12] It consists of three consecutive chemical treatments in an NH_4OH solution to remove organic and metallic contaminants, an HF solution to remove the native oxide layer, and an H_2O_2/HCl solution to remove alkali anions and metallic cations, and to produce a well-defined thin Si oxide layer. To yield a H-passivated surface, the samples of the corresponding series were dipped in an HF solution immediately before transferring them into UHV. Before BeTe overgrowth, the H passivation was removed by heating to 500 °C,[13] with the desorption process being controlled by reflection high-energy electron diffraction (RHEED).[14]

For the preparation of the As-passivated substrates, the Si samples were transferred into UHV after the RCA etch, and the oxide was removed by heating to 850–950 °C. After transfer to the III-V growth chamber, the samples were heated to 700 °C, cooled under As flux down to 300 °C to obtain the As passivation,[15] and exposed to As again at a temperature of $\sim -15\,°\mathrm{C}$ to deposit a protective cap. This cap allowed the samples to be transferred in air. Prior to BeTe overgrowth, the As cap was removed by heating to about 330 °C, while the As passivation remained on the sample, as will be discussed in Sec. IV.

BeTe was grown at a sample temperature of 330 °C, using separate Be and Te cells. We employed an extremely Te-rich growth regime with beam equivalent pressures of $1-2\times10^{-6}$ mbar (Te) and $1-2\times10^{-8}$ mbar (Be), respectively, opening the Te shutter 1 s before the Be shutter to ensure a Te-rich growth start. For reference purposes, one BeTe sample was prepared on a GaAs(100) substrate, yielding a BeTe(100) surface. The GaAs substrate was prepared as described in Ref. 10. All sample preparations were monitored *in situ* by RHEED whenever possible, in some cases being limited by geometric considerations when growing on sample holders compatible with the photoemission setups. In these cases standard preparation procedures were followed, which, on the commonly employed large sample holders, exhibit high crystalline surface qualities. The clean Si(111) surfaces exhibited a (7×7) reconstruction with sharp spots, and the BeTe(100) surfaces were (2×1)-reconstructed.

After growth, the samples were transferred in UHV transfer boxes (pressure better than 3×10^{-9} mbar) from the MBE system in Würzburg to different PES instruments at the synchrotron radiation sources BESSY I and II (Berlin, Germany) and to a local spectroscopy chamber. At BESSY I, photoelectron spectra were collected at a toroidal grating monochromator (TGM-1) using an angle-resolving electron spectrometer and photon energies between 13 and 120 eV. It had a combined energy resolution of monochromator and electron spectrometer between 0.15 and 0.4 eV, depending on photon energy. The PES experiments at BESSY II were performed at the U49/1-PGM undulator beamline with a Scienta SES 200 analyzer using photon energies between 460 and 1100 eV. The combined resolution (monochromator and analyzer) was better than 0.2 eV at $h\nu=700$ eV. The recently reported detector nonlinearities at low count rates[16] have been carefully corrected. The local PES setup consists of a Mg $K\alpha$ source, a gas discharge lamp for He I and II excitation (21.2 eV and 40.8 eV, respectively), and a VG MK II electron analyzer. All photoelectron spectra were taken in normal emission geometry. Special care was taken in cross-checking the energy scale calibrations between all three experimental setups. In all experiments, surface cleanliness was confirmed by XPS or Auger electron spectroscopy. The structural order of the surface was checked by RHEED during MBE growth (see above) and by low energy electron diffraction on selected samples after the experiments.

III. *k*-RESOLVED DETERMINATION OF THE VALENCE BAND MAXIMUM

We determined the valence band offset (VBO) based on the method first established by Grant, Waldrop, and Kraut[17] and Kraut *et al.*[18] Some details of our approach are discussed in Ref. 10. The original approach in Ref. 18 to determine the energetic position of the valence band maximum (VBM) in the PES spectra is based on a *k*-integrated measurement. The valence band (VB) edge as measured with an excitation on the order of $h\nu\sim1$ keV is scaled to coincide with a theoretical density of states (DOS) function, thus giving the position of the VBM in the spectrum. Because such an approach is limited by the availability of suitable calculations, we have additionally employed a *k-resolved* approach here. A suitable uv photon energy was chosen such that, according to the unoccupied band structure,[19] an excitation of the states at the VBM is possible, i.e., that the corresponding final state exists and that the involved matrix element is nonzero.[20,21] This leads to a maximized contribution from the VBM in the recorded VB spectrum. The position of the VB edge is then evaluated by linear extrapolation. The validity of this approach has already been demonstrated for a number of other systems, also in combination with inverse photoemission (IPES) experiments to determine the conduction band minimum and thus the bandgap.[10,20,21,22] In the case of zinc blende CdSe, it was also compared with the above discussed *k*-integrated approach.[23]

In order to demonstrate the quality of the *k*-resolved approach in our case of BeTe, we have investigated three samples, namely 25 nm BeTe/GaAs(100), and 10 and 40 nm BeTe on Si(111)-(H). Figure 1 depicts the corresponding spectra of the VB edge together with the Te $4d$ core levels, with the energy scale of the spectra given relative to the position of the Te $4d_{5/2}$ level. The energetic position of this

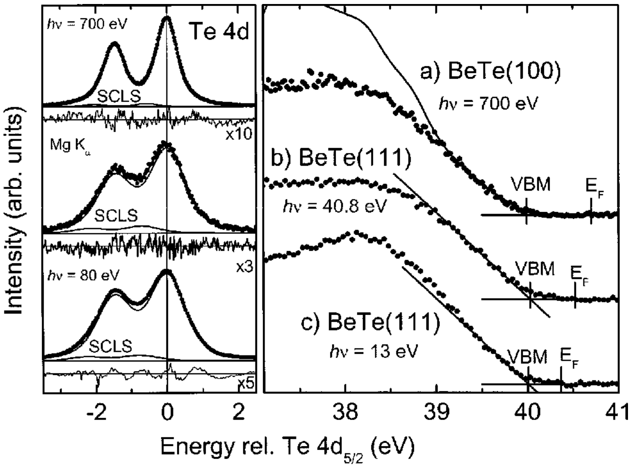

FIG. 1. BeTe valence band maxima (VBM) and Te 4d levels of 25 nm BeTe(100)/GaAs(100) (a) as well as 10 nm BeTe, (b) and 40 nm, (c) BeTe(111) on Si(111) prepared by desorption of a H passivation [Si-(H)]. The Te 4d core levels have been fitted with a linear background and two double Voigt functions to take spin-orbit splitting as well as a (weak) surface core level-shifted component (SCLS) into account. Beneath each spectrum the residuum is given, i.e., the enlarged (factors are given) difference between the spectrum and the fit. The VBM have been evaluated by a density-of-states fit (a,$h\nu = 700$ eV), or by a linear extrapolation of the valence band edge (b, $h\nu = 40.8$ eV, and c, $h\nu = 13$ eV). The experimental parameters and results are summarized in Table I.

reference level has been determined by fitting two double Voigt functions on a linear background, taking a spin-orbit splitting of 1.48 eV (determined from separate measurements) as well as a surface core level shift (SCLS) into account. Beneath the Te 4d spectra and the fits, the residuum, i.e., the (enlarged) difference between both, is shown. The VB edge of BeTe(100) [Fig. 1(a)] has been measured at a photon energy of 700 eV (i.e., following the k-integrated approach) and fitted with a theoretical DOS function which was Gaussian broadened to take the instrumental resolution into account. The DOS has been calculated by density functional theory in the local density approximation using *ab initio* pseudopotentials (for details see Ref. 24). For spectra (b) and (c) [BeTe on Si(111)-(H)], we chose excitation energies of 40.8 eV (He II excitation) and 13 eV, respectively, and determined the VBM position by linear extrapolation. The corresponding core levels have been measured using Mg $K\alpha$ and $h\nu = 80$ eV excitation, respectively.

The experimental parameters and results of the VBM determination are summarized in Table I. We find that the positions of the VBM relative to the Te 4d levels of all samples agree extremely well, yielding values between 39.99 and 40.03 eV, with an average value of 40.01 eV ± 0.05 eV. This agreement confirms the compatibility of the two determination approaches in the present case.

Concerning the surface orientation of the investigated samples, the energetic separation between VBM and core level(s) is independent of the surface orientation, as expected for a bulk property. On the other hand, since PES is a surface sensitive method, the determination of the energetic position of the VBM could be influenced by surface effects. Nevertheless, we observe the same VBM–Te 4d separation for both, the (100) and (111) orientation. Note that the position of the VBM relative to the Fermi level (as determined by a Au-foil reference), marked E_F in Fig. 1, is not constant, but varies between 0.36 and 0.71 eV (±0.05 eV; Table I). This is due to the dependence of the Fermi level position on surface dipoles, band bending effects, and the doping of the semiconductors.

To determine the VBM of the Si substrate, we used an As-passivated Si(111) sample and measured at an excitation energy of 21.2 eV (He I) in the k-resolved approach. The As surface passivation leads to the suppression of surface states,[25] which otherwise could disturb the correct determination of the VB edge. A linear extrapolation of the VB edge (not shown) leads to a VBM position relative to the Si 2$p_{3/2}$ level of 98.94 ± 0.07 eV. The corresponding core level spectrum, taken with Mg $K\alpha$ radiation, and the fit are shown in Fig. 2 (top left; the other spectra will be discussed in Sec. IV). From the fit, the existence of an interface core level shift (ICLS) due to Si–As bonds is derived, in accordance with Ref. 26. The spin-orbit splitting of the Si 2p levels of 0.605 ± 0.010 eV used in this fit was determined from a high-resolution spectrum at $h\nu = 700$ eV of a H-passivated Si(111) sample.

IV. VALENCE BAND OFFSET DETERMINATION

To determine the VBO of the BeTe/Si heterojunction, fits of all measured core levels of all samples [including the samples consisting of a "thin" BeTe overlayer on Si-As or Si-(H) substrates] were performed using a linear background.

TABLE I. Experimental parameters and VBM positions (relative to the Te 4$d_{5/2}$ level and the Fermi energy) for the data presented in Fig. 1. Both the k-integrated and k-resolved approach as well as both investigated surface orientations result in well agreeing values for the VBM relative to the Te 4$d_{5/2}$ level. In contrast, the position of the VBM relative to the Fermi energy varies since it depends, among others, on surface band bending and doping.

Sample	$h\nu$ (eV)	Determination of VBM	VBM rel. to Te 4$d_{5/2}$ (±0.05 eV)	VBM rel. to E_F (±0.05 eV)
(a) 25 nm BeTe/GaAs(100)	700	k integrated	39.99 eV	0.71 eV
(b) 40 nm BeTe/Si(111)-(H)	40.8	k resolved	40.03 eV	0.49 eV
(c) 10 nm BeTe/Si(111)-(H)	13	k resolved	40.01 eV	0.36 eV

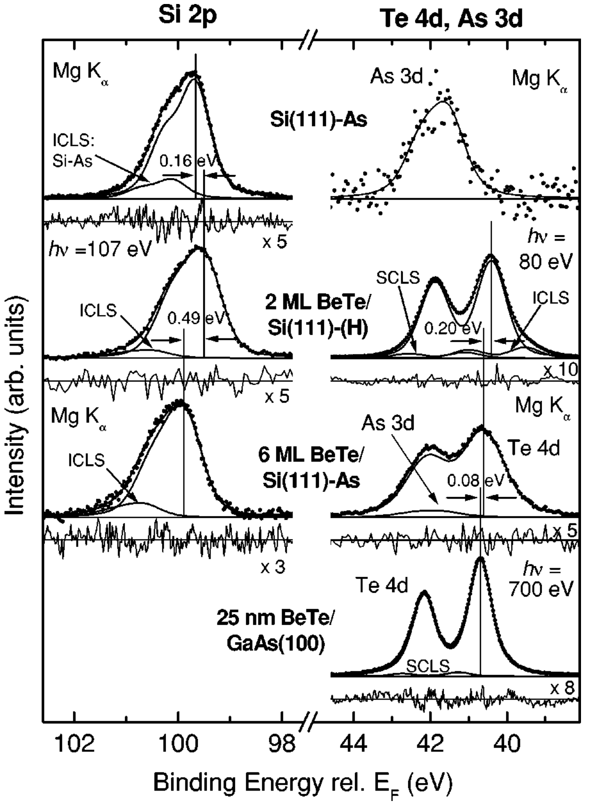

FIG. 2. Core level spectra and fits of an As-passivated Si(111) substrate (top), two samples of "thin" BeTe layers on Si(111)-(H) and Si(111)-As (2 ML and 6 ML, respectively; middle spectra), and a sample of "bulk" (25 nm) BeTe(100) on GaAs(100) (bottom). The amplified residua and their magnifaction factors are given beneath each spectrum. Surface and interface core level-shifted components are labeled SCLS and ICLS, respectively.

Figure 2 shows a selection of the spectra and fits. The band offset analysis is based on the Si $2p$ levels and the Te $4d$ levels. Note that the As $3d$ and Te $4d$ levels have approximately the same binding energy, but may easily be separated: As can be seen in the spectrum of 6 monolayer (ML) BeTe/Si-As in Fig. 2, the separation of the two peaks clearly corresponds to the Te $4d$ spin-orbit splitting of 1.48 eV, not to the As $3d$ splitting of 0.71 eV (which is not resolved). Fitting the Te $4d$ and As $3d$ levels with two double Voigt functions with fixed spin-orbit splitting and fixed area ratios (3:2) leads to a purely statistical residuum as depicted in Fig. 2 (right, 2nd spectrum from bottom). The small spectral As $3d$ contribution ($\sim$6%) is in good accord with the attenuation of an As signal stemming from an As monolayer buried by 6 ML BeTe.

By analyzing the Si $2p$ levels of the samples consisting of "thin" BeTe/Si (Fig. 2, left), an additional component at the high binding energy side is found which we attribute to an interfacial component, i.e., a chemically shifted core level due to Si–Be or Si–Te bonds at the interface. Furthermore, to obtain a satisfactory fit result, a SCLS at the high binding energy side had to be included for the Te levels of the BeTe overlayer in the same way as for the bulk BeTe samples described in Sec. III. In the case of 2 ML BeTe/Si-(H), a shoulder on the low binding energy side of the spectrum had to be taken into account, possibly arising from a core-level shift due to Si-Te interface bonds. This may significantly contribute to the spectrum of this sample due to the small overlayer thickness, and may be absent in the 6 ML BeTe/Si-(H) spectrum due to the thicker overlayer and/or the As interfacial layer.

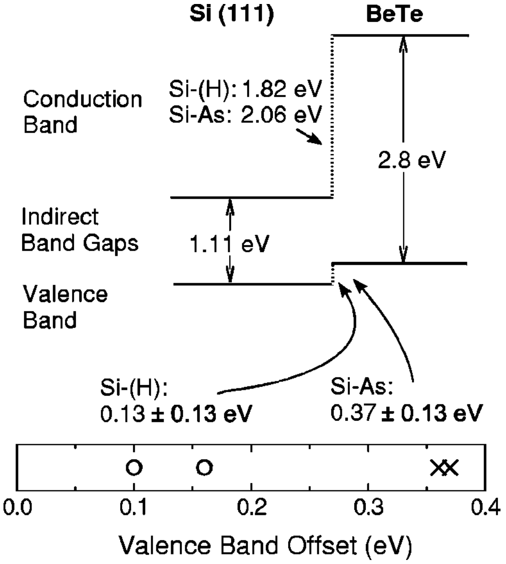

FIG. 3. Valence band offsets for all measured samples (bottom) and resulting band scheme (top) for BeTe on Si(111)-(H) and on Si(111)-As. The corresponding conduction band offsets have been calculated using literature values for the indirect band gaps (Ref. 1).

When evaluating the valence band offsets for both series [As-passivated and Si-(H) substrate], we find that the VBO is significantly higher in the case of Si-As as compared to Si-(H). For BeTe/Si-As, the average VBO is 0.37 ± 0.13 eV, while for BeTe/Si-(H) it is 0.13 ± 0.13 eV. The results for all measured samples, together with the resulting band scheme, are summarized in Fig. 3. The conduction band offsets of 2.06 eV (Si-As substrate) and 1.82 eV [Si-(H) substrate] have been deduced from our experimental VBO's using literature values for the indirect band gaps. Note that the conduction band minima of Si and BeTe are located at different points in reciprocal space. Hence, the here-derived CBO pertains to an "indirect band offset" (in analogy to an "indirect band gap" in semiconductors). This means that the details of the electronic transport across the interface are more complicated than in a simple band alignment picture. For an electron near the X point (i.e., near the CBM) of BeTe, the effective CB offset for transport without an additional scattering process is smaller than the indirect one. This is due to the fact that the CBM of Si is located between the Γ and the X point and that the (lowest) conduction band disperses upwards towards the X point. In contrast, the offset for an electron stemming from the CBM of Si is significantly increased.

We thus find that while electron conduction in the conduction band across the interface is difficult, the valence band shows only small barriers for hole conduction, particularly in the case of H passivation. This is favorable in view of the good *p*-doping possibilities of BeTe by nitrogen.[5] For the case of a $Be_{1-x}Mn_xTe/Si(111)$ spininjection device,[27] however, this is in contrast to the desire to utilize electron conduction due to the better spin coherence of electrons.[28]

V. DISCUSSION OF THE INTERFACE STRUCTURE

The fact that the VBO on unpassivated Si is significantly lower than for BeTe/Si-As indicates a strong influence of the substrate preparation method on the band offset. Note that, apart from the As passivation, all samples have been grown under identical conditions. Due to the high stability of this passivation layer and based on our PES data (see also Fig. 2), we find the As to remain at the interface even when the Si substrate is overgrown with BeTe. This is corroborated by a recent Raman experiment on Si(111)-As, which shows that the Raman resonance of the As monolayer is conserved when overgrown with Te or CdTe.[14,29] We conclude that the difference in band offsets stems primarily from the presence (or absence) of the arsenic passivation and thus from As atoms being built into the interface. This conclusion is corroborated by the fit result of Fig. 2 showing a residual As signal which is consistent with As atoms buried under 6 ML BeTe (see Sec. IV).

In general, heterovalent polar interfaces are intermixed due to the otherwise unbalanced number of valence electrons.[9] Thus they set up interface dipoles which can strongly influence the band offsets.[30] Because this intermixing is a very sensitive, sometimes metastable process, different samples prepared under nominally the same growth conditions may show a strong scatter of their band offsets,[8,20] for example, over an interval of 0.25 eV in the case of ZnSe/GaAs(100).[8] Our BeTe/Si samples, however, show a very small difference between the two different samples within each series [0.06 eV for BeTe/Si-(H) and 0.01 eV for BeTe/Si-As]. We ascribe this to the very Te-rich film growth condition, leading to an electronically well-defined, Te-rich interface in both cases (compare Refs. 8 and 20).

The exact interface structure cannot be derived from our photoemission data. However, at least for the unpassivated Si case, one is able to construct a possible interface model using the electron-counting rule.[31] According to the number of valence electrons distributed on the four bonds of the tetrahedrically bound atoms, a Te–Si bond has an excess of half a negative elementary charge, whereas the Be–Si bond has half a positive charge. Therefore, a possible interface structure would consist of Te replacing one of four Si top layer atoms (thus yielding three bonds to Si with a total of 1.5 negative elementary charges). The other three top layer Si atoms bond to one Be atom each, giving a total of 1.5 positive elementary charges, thus leading to a surface of neutral charge. The resulting strong interface dipoles cause a very small VBO, similar to, but stronger than, the dipoles at the group VI-rich ZnSe/GaAs interface.[8] This agrees very well with the present data.

In the case of the As-passivated substrate, a similar construction of the interface structure is more difficult for the following reason. Among the As bonds, only As–Be leads to a positive charge, whereas the As–Si and As–Te bonds both yield negative charges. Therefore, an As- *and* Te-rich interface possesses uncompensated negative charges, which leads to the conclusion that a Te-rich interface layer (obtained by the Te-rich growth start employed in our study) and an As interlayer (originating from the substrate passivation) counteract each other on the basis of electron counting arguments. Thus, constructing an interface model for this case is conceptionally difficult. For an exact determination of the interface setups, more appropriate theoretical tools are necessary.

Some experimental input can be expected from a study of the BeTe surface termination, because the Be/Te layer sequence is conserved during the growth on Si(111). While we indeed observe a SCLS for the Te 4*d* levels, the Be 1*s* peaks are very broad and do not lend themselves to an unambiguous determination of the surface termination. Thus, a structural study of the surface of BeTe/Si(111) would be desirable.

VI. SUMMARY

We have conducted photoelectron spectroscopy experiments on the BeTe/Si(111) interface to investigate the electronic and chemical interface structure and the impact of substrate passivation by As. Interfaces with As passivation were compared with those grown on unpassivated substrates, prepared by successive adsorption and desorption of a H passivation. In determining the valence band maximum of BeTe, we find that both the *k*-resolved approach (employing selected uv excitation energies) as well as the *k*-integrated approach (using x-ray excitation with $h\nu \sim 1$ keV) lead to well-matching results in the present case, even for different surface orientations.

The valence band offset of BeTe/Si depends significantly on the surface preparation, with an offset of 0.13 ± 0.13 eV for unpassivated Si and 0.37 ± 0.13 eV for As passivation. Together with the good reproducibility of the results, most likely achieved by a Te-rich growth leading to a well-defined interface structure, BeTe growth on H-passivated Si(111) is a promising candidate for well-defined heterostructures for hole conduction. The conduction band offsets for both preparation methods lead to offsets of about 2 eV and thus suggest the use of this system as quantum well structures. However, the employment of a $Be_{1-x}Mn_xTe/Si(111)$ structure for spin-injection purposes is more difficult due to the high conduction band offset obstructing the transport of spin-polarized electrons.

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