Rebonding at coherent interfaces between rocksalt-PbTe/zinc-blende-CdTe

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Abstract. We study interfaces between highly ionic crystals with different crystal structure by means of first-principles total-energy calculations in the repeated-slab approximation, and compare the results with experimental data extracted from high-resolution transmission electron micrographs. Despite the same Bravais lattices and the electrostatic neutrality of each atomic plane, the (110) interface between rocksalt and zinc-blende crystals gives rise to the most remarkable effect, a lateral spatial offset between the two crystals due to rebonding across the interface. A strong variation is observed for the separation of the two polar (001) interfaces depending on their cation- or anion-termination. In general, the long-range electrostatic forces lead to opposite atomic displacements along the interface normal independently of the interface orientation.
1. Introduction

An important motivation for the development of semiconductor quantum-dot materials is the possibility to improve the efficiency of light-emitting devices. These improvements are based on the peak-like density of states of three-dimensionally confined carriers and the optimal overlap between the wavefunctions of electrons and holes trapped in the same quantum dots (QDs) [1]. However, by reducing the dimensions of the quantum devices, their performance is increasingly affected by the properties of the interfaces. For instance, QDs with inadequately passivated surfaces such as, e.g. most samples prepared in silicate glasses [2]–[4], typically emit from deep trap states with low quantum yield. Band-edge emission with high quantum yield is obtained from colloidal QDs [5] that are passivated by organic overlayers, as well as from dots fabricated by strain-induced heteroepitaxy [6]. The resulting Stranski–Krastanov [7] QDs are embedded in a matrix of the same crystal structure but with a larger band-gap energy. While for III–V [8] and II–VI [9] compound systems Stranski–Krastanov QDs with almost perfect optical properties have been demonstrated, for IV–VI materials the situation is completely different. By combining PbSe with PbEuTe high-quality self-assembled QDs are formed, which exhibit exceptional topographical effects, such as the 3D ordering of the dots in superstructures [10]. These systems are, however, of limited applicability for light-emitting devices, because of the staggered type-II band alignment between the hydrostatically strained PbSe QDs and the PbEuTe matrix leading to spatially separated electrons and holes [11].

In contrast, a type-I offset for QDs based on lead salts could recently be demonstrated. The highly symmetric epitaxial PbTe dots embedded in a CdTe matrix are formed by thermally induced precipitation after growth. They exhibit an intense room-temperature photoluminescence in the mid-infrared spectral region [12]. PbTe nanocrystals and CdTe matrix possess the same face-centred cubic (fcc) translational symmetry, and almost identical lattice constants (theoretical values: 0.639 nm—PbTe, 0.642 nm—CdTe), but differ in their crystal structures, rocksalt (rs) and zinc-blende (zb), respectively. Despite the crystal-structure mismatch, coherent interfaces in all high-symmetry directions ⟨110⟩, ⟨001⟩ and ⟨111⟩ have been observed [12]. Because of the importance of the interfaces, and also because of the almost perfect match of the lattice constants, the PbTe/CdTe semiconductor heterosystem will be employed as a model system in the following. However, there are other prominent examples for this type of self-assembled nanostructures induced by the immiscibility of rs and zb lattices. For instance, the properties and potential device applications of the semimetal ErAs(rs) in either a AlAs(zb) [13, 14] or a lattice-constant matched In_{0.53}Ga_{0.47}As(zb) matrix [15].
The discussed heterostructures between rs and zb crystals contain new types of interfaces. The adjacent crystals are not only compounds with different chemical properties but also possess different atomic geometries and bonding arrangements. A severe mismatch of the dangling bonds at the interface is expected with respect to position, orientation and hybridisation. This becomes evident by considering that the rs structure of PbTe is 6-fold coordinated, whereas in the zb structure of CdTe each atom has only four nearest neighbours. In addition, a polarity mismatch arises due to the polar \{001\} faces of the zb structure in combination with the neutral faces of the rs structure. Hence, for a (001) interface with constant anion sublattice on both sides two different interface types occur \[13, 16, 17\], depending on the cation- or anion-termination of the zb(001) surface. The only non-polar zb face is the (110) cleavage plane, which is also electrostatically neutral in the rs case. A fundamental understanding of the chemical bonding and the resulting geometries is missing for the rs/zb interfaces with crystal-structure mismatch.

In the present paper, we concentrate on the structural properties of the (110) and (001) interfaces between PbTe and CdTe as prototypical interfaces between two different polymorphs of different compounds. To obtain the atomic equilibrium positions we apply a total-energy (TE) minimization scheme based on first principles. The results are quantitatively compared with high-resolution transmission electron microscopy (HRTEM) images and corresponding multi-slice simulations. We investigate how covalent or ionic rebonding across the interfaces influences the positions of the atoms in the transition regions or even the relative arrangement of the two macroscopic crystals with different geometry. We discuss the effect of the long-range electrostatic forces, the tendency to continue the crystal structure also in the adjacent compound and the relative positions of cation and anion sublayers with respect to the interface. The effect of the cation- or anion-termination of a polar (001) interface on its spatial separation is studied in detail.

2. Theoretical method

For the TE calculations we apply the density functional theory (DFT) in local density approximation (LDA) as implemented in the Vienna \textit{ab initio} simulation package (VASP) \[18\]. Besides the outermost \(s\) and \(p\) electrons also the shallow semicore Cd4\(d\) and Pb5\(d\) electrons are taken into account. The interaction of all the valence electrons with the ions is modelled by pseudopotentials generated within the projector–augmented wave (PAW) method \[19\]. The radii of the augmentation spheres are 0.12, 0.13, 0.12 nm for Te, Pb and Cd respectively. Tests showed that an energy cutoff of 15 Ry for the plane-wave basis is sufficient for convergence of the TE, i.e. a further increase of the basis set will result in a TE change of less than 1.5%. However, the influence of the cutoff energy on the interface displacements is negligible within the accuracy requirements. The Brillouin-zone summations are restricted to \(5 \times 7 \times 1\{110\}\) and \(7 \times 7 \times 1\{001\}\) meshes of special points according to Monkhorst and Pack \[20\]. The modelling of the interfaces is based on the repeated-slab approximation \[21\]. The small lattice-constant mismatch is neglected, and an average (theoretical) of \(a_0 = 0.641\) nm is assumed. Since the deviations from the bulk lattice constants of about \(-0.002\) nm (PbTe) or \(0.001\) nm (CdTe) are small against the displacements discussed below no further relaxation of the supercell volume has been allowed. Each material slab consists of the same number of cations and anions. In order to reduce the interaction of the two interfaces in a supercell we use seven irreducible crystal slabs \[21\] for both the \{110\} and \{001\} orientations. Each irreducible slab consists of four atomic layers.
3. Experimental set-up

The samples for the HRTEM investigations were grown by solid-source molecular beam epitaxy (MBE) on a GaAs(001) substrate. First, a 900 nm thick, Cd-stabilized CdTe layer with a buried CdTe/MnTe superlattice was grown as a high-quality metamorphic buffer layer, which was followed by pseudomorphic low-temperature (250 °C) deposition of a thin (3–10 nm) PbTe layer and a 50 nm thick CdTe capping layer [22]. HRTEM images reveal [12] that the as-grown samples contain coherent interfaces of both PbTe/CdTe(001) terminations. Post-growth annealing at different temperatures between 280 and 350 °C for 10 minutes in an inert-gas environment leads to a disintegration of the PbTe layer into PbTe QDs that are coherently embedded in the CdTe matrix. Depending on the thickness of the original PbTe layer, QD diameters vary between 6 and 25 nm. Cross-sectional HRTEM images were digitally recorded with a JEOL 2011FasTEM instrument under almost ideal defocusing conditions at 200 keV along the [\(\bar{1}10\)] zone axis. For a quantitative extraction of the atomic displacements near the interfaces, we performed multi-slice Transmission electron microscopy (TEM) simulations utilizing the commercial JEMS code. TEM investigations on several dozen QDs in more than ten different samples show that the dots are centrosymmetric with almost atomically sharp interfaces. The dominating interface facets (figure 1(b)) are found to be \{001\}, \{110\} and \{111\}. Because of the different selection rules the rs and zb lattices can easily be identified in the HRTEM images: the former show resolved (002) and (220) lattice planes, whereas for the latter only two adjacent (111) planes are symmetry allowed, as indicated in figure 1(b).
4. Discussion

Minimization of the TE results in geometrical changes of up to about 10% of the lattice constant. For the PbTe/CdTe(110) interface the accompanying valence electron density is represented in figure 2. We have chosen a (110) plane which contains zigzag chains of mixed covalent-ionic bonds in zb-CdTe related to the \( sp^3 \) hybridization of the atoms. There is a tendency to continue such a chain into the rs-PbTe due to the formation of a more covalent bond directed along \([-\bar{1}1\bar{1}]\) between a Cd atom of CdTe and a Te atom of PbTe. With the centre of charge density distribution along the bond closer to Te the 1/2 electron from the Cd\( sp^3 \) hybrid may contribute to complete the valence shell of the Te atom which misses 1/3 electron at the free rs (110) surface. The formation of such interface bonds with 4-fold coordinated Cd atoms does not require displacements of the participating atoms. From the point of view of the \( p \)-bonded Te interface atoms at the rs side, the adjacent Cd atoms at the zb side have to be displaced from their \((1, 1, \bar{1})\frac{a_0}{4}\) positions to \((1, 1, \bar{1})\frac{a_0}{2}\) in order to achieve a 6-fold coordination. However, this tendency is weak because of the less directional character of the ionic bonds in a rs-like environment.

The interplay between the two tendencies results in significant atomic displacements at a non-polar (110) interface, as shown in figure 3. The most prominent effect is a collective shift of all ions by \(- (0, 0, 0.020) + (0, 0, 0.018) \) nm on the CdTe and the PbTe side, respectively. This results in an substantial offset between the Te fcc sublattices on either side of the interface of 0.038 nm along the [001] direction. An important reason for the offset is indicated in figure 2. The Cd atoms in the interface tend to occupy a 4-fold-coordinated site by forming a bond along the [1\bar{1}1] direction to a Te atom of PbTe. In addition, there is a repulsion between the Pb and Cd atoms across the interface. Normal to the interface the displacements are small, but show an interesting behaviour for atoms of the PbTe slab. They describe an oscillating relaxation, similar to that found for the PbTe(001) surface, known as the rumpling effect [21, 23, 24]. It results in

**Figure 2.** Valence electron density (restricted to values between 260 and 600 nm\(^{-3}\) to enhance the resolution) in a (1\bar{1}0) plane around the PbTe/CdTe(110) interface with indicated atomic positions: Te (yellow), Cd (red), Pb (green). The colour scale varies from blue (vanishing density) to red (very high density). The vertical line indicates the nominal interface position.
Figure 3. Atomic displacements calculated in a PbTe/CdTe(110) supercell (shown) and the ones measured near the interfaces. The displacements are given parallel to [001] (red squares, calculated; red up triangles, measured) and [110] (green diamonds, calculated; green down triangles, measured) for the equivalent (110) interfaces. Displacements in other directions do not occur. The two nominal interfaces in the supercell are indicated by vertical lines.

A weak splitting of the neutral PbTe(110) planes into bilayers. The effect vanishes in the slab centre and increases toward the interfaces. For both Pb and Te, it is smaller than the averaged displacement of neighbouring layers. The split bilayers change the polarity in an oscillating manner, so that the total electrostatic energy of the system is reduced.

The prediction of an almost ideal (110) interface between rs- and zb-crystals of nearly the same lattice constant and, in particular, of the finite offset of the crystal halves at the interface was checked with HRTEM. Figure 4(a) shows a representative image of this interface with PbTe on the left panel; the locations of the electron clouds correspond to the dark areas. Evidently, the interface is almost atomically sharp, and a small offset of the two crystal halves in the [001] direction can be seen even in the raw image. To quantify the atomic displacements we performed TEM multi-slice simulations, which provide the atomic positions indicated in figure 4(b). To allow for direct comparison, the experimental results are added to figure 3, revealing excellent agreement with the TE calculations. This holds not only for the signs but also for the absolute values of the displacements near the (110) interfaces. The lateral spatial offset parallel to [001] of about 0.038 nm between the Te sublattices and (apart from the PbTe side) almost vanishing normal displacements are clearly confirmed. The relatively large lateral Pb displacements of about 0.04 nm and their decrease away from the interface are results of both methods. There is good agreement with experiment, taking into consideration the limitations of the slab method due to finite material layers and of the multi-slice TEM simulation with its precision and the need for starting coordinates.
Figure 4. TEM images of the CdTe/PbTe(110) interface along the [1 1 0] zone axis. (a) experimental HRTEM images. (b) multi-slice TEM simulation with indicated atomic positions. The different circle sizes represent atoms in different layers perpendicular to [1 1 0]. (c) stick-and-ball model of a PbTe/CdTe(110) interface.

The HRTEM images for the two PbTe/CdTe(001) interfaces, which differ according to the Cd- or Te-termination of the CdTe(001) half space, are shown in figure 5. They are compared with atomic positions obtained from TE calculations. In both cases only normal displacements along [001] occur. The combination of a non-polar (001) surface of rs-PbTe with a polar (001) (i.e., Cd-terminated) or (001) (i.e., Te-terminated) surface of zb-CdTe gives rise to completely different interfaces with respect to spatial separation and bonding behaviour. The Cd-termination tends to a continuation of the zb-structure across the interface leading to an interface separation of nominal $a_0/4$. TE calculations (concerning different interface separations) reveal that this ideal value is increased by 0.03 nm. This may be interpreted by overlapping of one Cd$sp^3$ dangling hybrid of the CdTe(001) surface with a Te $p$-orbital from the other side. However, even a full ionization of the interface Pb atom transferring 1/3 electron to the neighbouring interface Te atom cannot yield a strongly covalent bond occupied with two electrons. On the other hand, the Te-termination of the zb-crystal tends to a continuation of the rs-structure across the interface resulting in a nominal separation of $a_0/2$, reduced by 0.005 nm. The bonding of the two crystals is dominated by electrostatic interactions. The rs(001) face with one $p$ dangling orbital per atom with opposite ionic charges and thus global electrostatic neutrality is rather stable. Moreover, the Te atoms of the zb side with two $sp^3$ dangling hybrids possess already a high probability of finding seven electrons near them. The ab initio calculated atomic positions clearly follow this bonding picture.

The two different (001) interface structures are clearly confirmed by the HRTEM images as shown in figure 5. In particular, for the Te-terminated interface (a) we tested different assumptions about the geometry. The best agreement is found for the theoretical predictions. The most important result is the clear confirmation of the different separations of the Cd- and Te-terminated interfaces. On the other hand, the small atomic displacements along the interface normal including the rumpling effect on the PbTe side are hardly visible.
5. Summary

In summary, we studied in detail the structural properties of coherent interfaces between cubic crystals with different crystallographic structure and rather strong ionic bonding contributions. As a model system, we combined rs-PbTe with zb-CdTe, which have almost identical lattice constants. To clarify the rebonding at the interfaces we compared the results of \textit{ab initio} calculations with those of HRTEM. For the absolute atomic positions we demonstrated not only qualitative but also quantitative agreement. At \{110\} interfaces between two non-polar faces of the zb and the rs structure we found a lateral offset between the two crystals. This effect is mainly a consequence of the formation of a covalent bond across the interface. At \{001\} interfaces between a polar and a neutral face the bond lengths across the interface depend on the termination of the CdTe crystal. For both orientations the rebonding at the interface can be traced back to the interplay between a tendency for more directional bonds (as in the 4-fold coordinated CdTe), and for more isotropic electrostatic interactions (as in the 6-fold coordinated PbTe).

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