

Hexagonal Ge/Si_{0.25}Ge_{0.75} quantum wells: Prediction of quantization and light-emission strengthAbderrezak Belabbes^{1,2,*}, Martin Keller², Jürgen Furthmüller², Silvana Botti^{3,2} and Friedhelm Bechstedt²¹Department of Physics, Sultan Qaboos University, P.O. Box 36, PC 123, Muscat, Oman²Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany³Research Center Future Energy Materials and Systems, Interdisciplinary Centre for Advanced Materials Simulation, Faculty of Physics and Astronomy, Ruhr University Bochum, Universitätsstrasse 150, 44801 Bochum, Germany

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We investigate heterostructures composed of hexagonal Ge quantum wells embedded within hexagonal Si_{0.25}Ge_{0.75} alloy layers, systematically considering variations in crystallographic orientation, well thickness, and external biaxial strain. This study employs density functional theory together with accurate functionals for calculations of the quasiparticle electronic structure. Overall, the heterostructures exhibit type-I band alignment, with the localization of electron and hole wave functions predominantly within the hexagonal Ge regions. The quantum confinement of both charge carrier types is determined by the orientation and thickness of the Ge layer for three different external strains. The results obtained can be interpreted within a rectangular potential-well model, with characteristic parameters derived from *ab initio* band structures of hexagonal Ge and Si_{0.25}Ge_{0.75}, as well as their strained multiquantum well structures, properly aligned via the branch point energies. Besides confinement energies and subbands, optical transition strengths are also discussed.

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I. INTRODUCTION

Heterostructures formed by cubic silicon (Si) and germanium (Ge), including their Si_xGe_{1-x} alloys, play a crucial role in microelectronic and photonic devices [1], with band-gap energies and valence- and conduction-band discontinuities significantly influencing their electronic and optical properties [2,3]. Electron or hole spins confined in top-gated Si and Ge quantum wells are excellent candidates for realizing reliable solid state based qubits [4–8]. The design of quantum devices relies on understanding how these properties are affected by factors such as strain and layer thickness [9].

Although heterostructures based on the diamond structure of Si, Ge, and SiGe are widely established, they face limitations in active optoelectronic applications such as lasers and light-emitting diodes (LEDs) [10]. Fortunately, recent breakthroughs have revealed efficient light emission from the direct band gap of lonsdaleite (2H) phases of Ge and Ge-rich Si_xGe_{1-x} alloys, particularly when grown on wurtzite III-V nanowires [11]. The efficiency of light emission can be enhanced by alloying [12,13], symmetry breaking [14], or strain [15].

Light efficiency and lasing characteristics can be improved in quantum well (QW) heterostructures [16]. This has recently been demonstrated for 2H-Ge wells embedded in 2H-Si_xGe_{1-x} ($x = 0.2$) barriers, obtained in multishell heterostructures grown on a wurtzite-GaAs nanowire substrate

with (1 $\bar{1}$ 00) facets [17]. In contrast to the case of cubic SiGe heterostructures [18–20], the present understanding of 2H-Ge/Si_xGe_{1-x} heterostructures is still rather limited. Some of us have recently published *ab initio* investigations of band alignments in 2H-SiGe heterostructures [21,22] grown in the [0001] direction. In this work, we study the electronic structure versus geometry and investigate the dependence of the interface band lineup with respect to controllable parameters such as interface orientation, well thickness, and external strain, as well as the quantization effects in QWs for electrons and holes.

To this end, we perform calculations of the structural and electronic properties of particularly promising [17] multi-QW structures made by lonsdaleite 2H-Ge embedded in hexagonal Si_{0.25}Ge_{0.75} by means of the density functional theory (DFT). In order to accurately describe the electronic structure and to enable calculations of supercells, we obtain approximate quasiparticle energy levels using the modified Becke-Johnson functional [23] with correlation in the local density approximation (MBJLDA). This meta-GGA functional proposed by Tran and Blaha [24,25] has been shown to produce excellent agreement with experimental band gaps and band structures for diamond Si and Ge [26], 2H-Si [12], 2H-Ge [12,27] and their alloys [11,12], and generally for semiconductors [28,29].

Our theoretical and numerical methods are outlined in Sec. II. In Sec. III we present a detailed examination and discussion of atomic geometries and band structures of 2H-Ge/2H-Si_{0.25}Ge_{0.75} multi-QW systems, exploring the impact on the electronic and optical properties of different interface orientations, layer thicknesses, and external strain. This comprehensive investigation enables us to derive effective gaps between electron and hole subbands, as well as band offsets. Additionally, we interpret quantization effects on electrons and holes in the QW region, employing effective

*Contact author: abderrezak.belabbes@uni-jena.de

mass theory (EMA) and rectangular potential wells. Finally, as presented in Sec. IV, we offer a thorough summary and draw conclusions from our findings. This includes a nuanced understanding of the intricate interplay between structural parameters and electronic properties in hexagonal Ge/Si_xGe_{1-x} heterostructures. The knowledge gained from these studies is anticipated to advance the development of efficient and tailored quantum devices for future technological applications.

II. METHODS

A. Atomic geometries

The ground-state properties were calculated in the framework of DFT as implemented in VASP [30,31] using the projector-augmented wave method [32] with a plane-wave cutoff of 500 eV. The shallow Ge 3*d* electrons are treated as valence states. The Perdew-Becke-Ernzerhof exchange-correlation (XC) functional revised for solids PBEsol [33] is used for geometry relaxations. For bulk hexagonal crystals with four-atom unit cells the Brillouin zone (BZ) integration is performed with a Γ -centered $12 \times 12 \times 6$ **k**-point grid. A full relaxation of the internal atomic positions of bulk hexagonal *m*-, *a*-, and *c*-plane interfaces was achieved by minimizing the Hellmann-Feynman forces acting on each atom to be less than 5 meV/Å. Total energy was converged within 0.5 meV/cell.

B. Electronic structures

All quasiparticle band structures are calculated using the MBJLDA XC potential of Tran and Blaha [24,25] that combines the modified Becke-Johnson (MBJ) exchange [23] with correlation in the local density approximation (LDA) [34]. Spin-orbit coupling (SOC) is always considered as the resulting corrections to the band structure are important for Ge and alloys with large Ge content.

The resulting band structure and density of states (DOS) for 2H-Ge (a) and the ordered alloy 2H-Si_{0.25}Ge_{0.75} (b), where one Ge atom is replaced by a Si one in the unit cell, are displayed in Fig. SM1 of the Supplemental Material [35]. The band structures are in agreement with previously published results [12,26,27]. They describe direct-gap semiconductors with the lowest gap energy at Γ . With the incorporation of 25% Si, the gap of about $E_g = 0.30$ eV of unstrained 2H-Ge is significantly opened to 0.53 eV. As a consequence, the energy splittings due to SOC and the hexagonal crystal field between the uppermost three valence bands are slightly increased. Their values are 0.12 and 0.43 eV, respectively, for 2H-Ge and 0.13 and 0.48 eV, respectively, for 2H-Si_{0.25}Ge_{0.75}. The distance between the two lowest conduction-band minima strongly increases from 0.35 in 2H-Ge to 0.94 eV in the 2H-SiGe alloy.

C. Quantum well structures

We restrict our consideration to Ge-rich hexagonal Si_xGe_{1-x} alloys, as a Ge content smaller than $x = 0.6$ leads to indirect band gap materials [12,13]. The interface between 2H-Ge and 2H-Si_{0.25}Ge_{0.75} has been identified as type I with natural band discontinuities of $\Delta E_c = 0.20$ eV ($\Delta E_v = 0.02$ eV) by some of us [21], using the branch-point

(BP) alignment [36]. This alloy composition is also close to the one realized in experiments [11,17].

We assume that the electronic structure of the alloy can be reasonably described by a four-atom lonsdaleite unit cell [12,13,21], where one atomic site is occupied with a Si atom instead of a Ge one. Under this assumption, the hexagonal *c* axis [0001] can be easily used to construct heterostructures with interfaces parallel to the *c* plane (see Ref. [21]) by arranging a number N_{Ge} of Ge₄ unit cells to a layer thickness $L_{\text{Ge}} = N_{\text{Ge}}c_{\text{Ge}}$ with the *c*-lattice constant $c_{\text{Ge}} = 6.5920$ Å and another number N_{SiGe} of Si₁Ge₃ unit cells to a layer thickness $L_{\text{SiGe}} = N_{\text{SiGe}}c_{\text{SiGe}}$ with the shorter *c*-lattice constant $c_{\text{SiGe}} = 6.5150$ Å [21]. Since, however, the in-plane *a*-lattice constants of 2H-Ge and the alloys $a_{\text{Ge}} = 3.9960$ Å and $a_{\text{SiGe}} = 3.9464$ Å are also different, the assumption of pseudomorphic growth of Ge and Si_{0.25}Ge_{0.75} on each other can be only realized by modifying the two in-plane lattice parameters to assume a common (relaxed) lattice constant *a*. This will induce a biaxial strain of opposite sign on the two sides of the interface, with a magnitude dependent on the layer thicknesses L_{Ge} and L_{SiGe} , as well as on the Young moduli Y_{Ge} and Y_{SiGe} [21]. The supercells obtained following this construction describe superlattices with lattice constants $L_{\text{Ge}} + L_{\text{SiGe}}$ (influenced by atomic relaxation and the Poisson effect) in the [0001] direction and an in-plane lattice constant equal to *a*. The supercells are hexagonal with a huge *c*-lattice constant. However, the symmetry of lonsdaleite Ge with space group $P6_3/mmc(C_{6v}^4)$ is reduced to $P3m1(C_{3v}^1)$.

The core-shell 2H-Ge/2H-Si_{0.25}Ge_{0.75} heterostructures grown on nanowire substrates made of wurtzite GaAs have interfaces oriented perpendicularly to the $[1\bar{1}00]$ direction, called *m*-plane interfaces (cf. Fig. 1 and Fig. SM2 of the Supplemental Material [35]). An external compressive, nearly biaxial strain acts in the plane perpendicular to the growth direction, resulting in a reduction of the *a*-lattice constant by -0.6% and of the *c*-lattice constant by -0.91% in the thinner 2H-Ge layer [17]. In the growth $[1\bar{1}00]$ direction the distances between the atomic layers however increase. Therefore, a nearly compressive hydrostatic strain can be simulated by fixing these layer distances by 0.6% shrunken values. The different orientation and the external strain have to be taken into account to build the supercell of the actually studied multiquantum well system. The resulting superlattices possess orthorhombic Bravais lattices with space group $Pmm2(C_{2v}^1)$. Other low-energy surfaces relevant for experimental QW heterostructures are the *a* plane [cf. Fig. SM2 (a) of the Supplemental Material [35]], perpendicular to the direction $[11\bar{2}0]$, or the *r* planes, perpendicular to the $[1\bar{1}00]$ or $[1\bar{1}02]$ directions. The corresponding supercells describe monoclinic Bravais lattices with space group $P2/m(C_{2h}^1)$. The relations of the 3D BZ of bulk lonsdaleite to the 2D BZs of *c*, *m*, and *a* interfaces are illustrated in Fig. SM2 (b) of the Supplemental Material [35].

III. RESULTS AND DISCUSSION

A. $(1\bar{1}00)$ quantum wells: Thickness and strain dependence

1. Geometries

We start considering 2H-Ge layers sandwiched by 2H-Si_{0.25}Ge_{0.75} layers using the description of a periodic

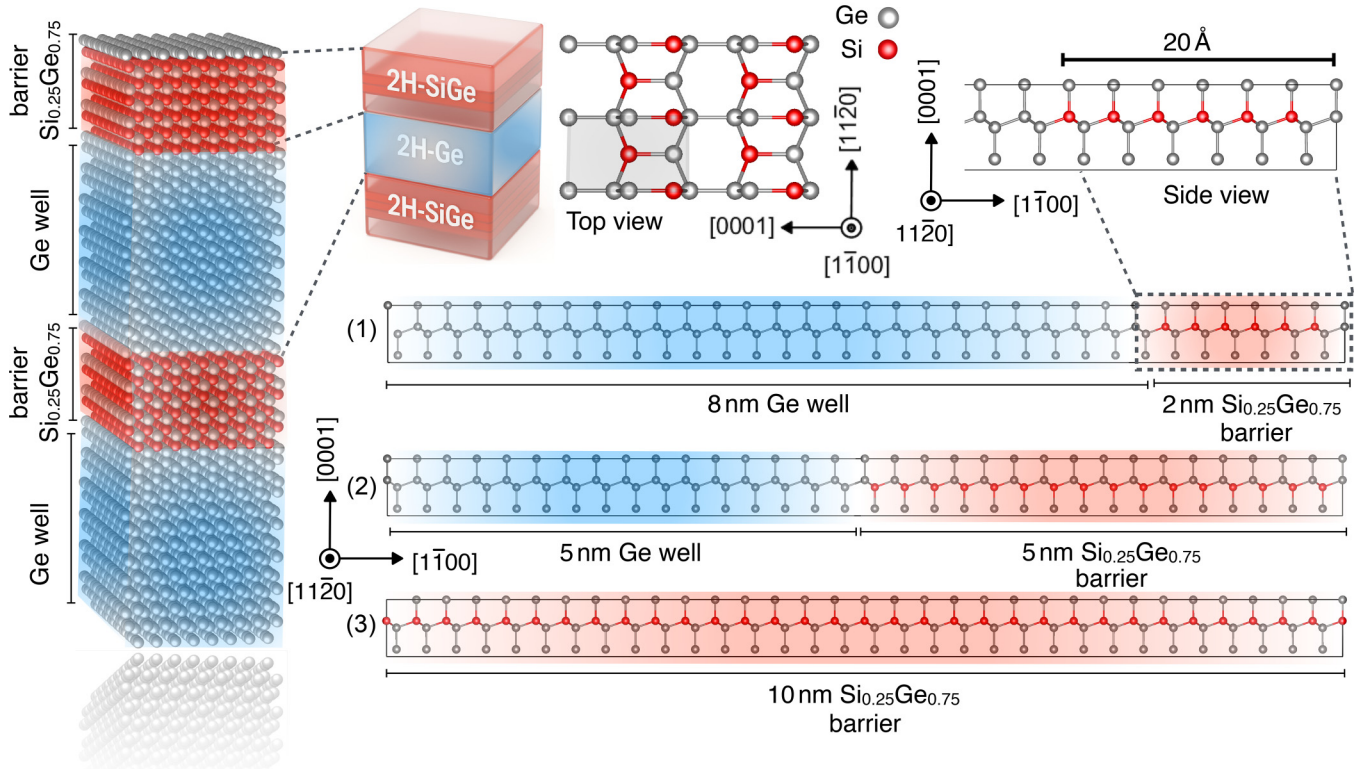


FIG. 1. Multi-QW structures used in the simulations (left panel). Side views of three typical 2H-Ge/Si_{0.25}Ge_{0.75}(1 $\bar{1}$ 00) orthorhombic superlattices with unit cells consisting of 32 bilayers—more precisely 26 (16, 0) Ge and 6 (16, 32) Si_{0.25}Ge_{0.75} bilayers for (1) [(2), (3)] (lower right part). Ge (Si) atoms are indicated by gray (red) circles. The top view on one bilayer is also displayed together with one lateral unit cell (gray region). For the superlattice (1) we also show a zoom in the Si_{0.25}Ge_{0.75} barrier layer together with the interface to the 2H-Ge well material.

superlattice with its axis along the $[1\bar{1}00]$ direction. These so-called m -plane superlattices (cf. Fig. 1 and Fig. SM2 of the Supplemental Material [35]) have orthorhombic (1×1) unit cells with crystal axes $\mathbf{a}_m$, $\mathbf{b}_m$, and $\mathbf{c}_m$. Three examples of such superlattices with a repeated unit of overall 32 hexagonal (bi)layers made of Si and Ge atoms with a nominal thickness of $\sqrt{3}a/2$, i.e., 128 atoms in the supercell, are illustrated in Fig. 1. The Ge-rich alloy region in each supercell is characterized by an ordered arrangement of the alloying Si atoms, with one Si atom in a four-atom bilayer subunit repeated in the $[1\bar{1}00]$ direction, where each subunit has edge lengths a_m and b_m that are given as $a_m = a$ and $b_m = c$ in the case of lonsdaleite crystals with lattice constants a and c . As a result, the Si atoms create lines along the $[1\bar{1}00]$ direction as illustrated in Fig. 1. We remark that we have considered the possible influence of the actual Si distribution in the alloy barrier material by performing calculations for other atomic orderings: a zigzag arrangement by changing the site of each second Si atom perpendicular to the superlattice axis and a pairing mechanism, introducing alternating pairs of neighboring Si and Ge atoms along the superlattice axis. For an 8 nm Ge/2 nm Si_{0.25}Ge_{0.75} multi-QW structure we only found a very minor, i.e., practically negligible, influence of the Si distribution on the electronic properties. The fundamental band gap of the alloy and the branch point energy, which influence the global electronic properties of the

heterostructure, only show maximum deviations of 5 meV with respect to their values in the geometry with a linear Si arrangement.

The supercells built with (1) 6 SiGe and 26 Ge bilayers, (2) 16 SiGe and 16 Ge bilayers, and (3) 32 SiGe and no Ge bilayers (i.e., pure alloy) are displayed in Fig. 1. In the free-standing case, without substrate, the atomic relaxation leads to lattice constants a_m of 3.9862 Å, 3.9648 Å, and 3.9449 Å, b_m of 6.5760 Å, 6.5429 Å, and 6.5175 Å, as well as c_m of 110.1601 Å, 109.7648 Å, and 109.3194 Å for the supercells (1), (2), and (3), respectively. The interface mismatch between the Ge and SiGe alloy layers leads to macroscopically compressive (on Ge) and tensile (on the SiGe alloy) biaxial strain. The supercell (3) describes the ordered alloy 2H-Si_{0.25}Ge_{0.75}. We also built an analogous orthorhombic supercell containing pure Ge, obtaining relaxed lattice constants of $a_m = 3.9910$ Å, $b_m = 6.5827$ Å, and $c_m = 110.5493$ Å. We conclude that the Ge layers undergo compressive biaxial strain of $\epsilon_{aa} = -0.12\%$ in the superlattice geometry (1) and -0.66% in the superlattice geometry (2) of Fig. 1. The corresponding tensile strains on the Si_{0.25}Ge_{0.75} materials are $\epsilon_{aa} = 1.04\%$ for the geometry (1) and 0.50% for the geometry (2), as well as $\epsilon_{bb} = 0.90\%$ for (1) and 0.39% for (2). In view of these values, considering typical deformation potentials [13,15,21], we expect drastic strain-induced changes in the band gaps and band discontinuities.

Since *ab initio* modeling becomes too computationally expensive for QW structures with too many atoms and we want to investigate well thicknesses up to 15 nm, we used the smallest possible size of the $\text{Si}_{0.25}\text{Ge}_{0.75}$ barrier that corresponds to negligible tunneling. In this sense, the used superlattices describe repeated isolated quantum wells. Our convergence tests demonstrated that a thickness L_{SiGe} of 2 nm, i.e., 6 bilayers (12 atomic layers) in the $[1\bar{1}00]$ direction, is sufficient to guarantee the localization of the wave functions of the lowest electron and the highest hole band in the 2H-Ge regions. Tunneling of these wave functions through the $\text{Si}_{0.25}\text{Ge}_{0.75}$ barriers is indeed found to be negligible [21]. The thickness L_{Ge} of the 2H-Ge layers is then varied in the wide range $L_{\text{Ge}} = 4, 6, 8, 11$, and 15 nm in order to explore the influence of the well thickness, interfacial strain, and quantum confinement of electrons and holes on the resulting energy levels.

We note that these calculations assume a pseudomorphic growth that gives rise to mutual strains in 2H-Ge and 2H- $\text{Si}_{0.25}\text{Ge}_{0.75}$ of the order of $-0.2 \dots -0.8\%$ and $0.5 \dots 1.0\%$, respectively, depending on the layer thicknesses. However, when the 2H-Ge/ $\text{Si}_{0.25}\text{Ge}_{0.75}$ QW structures are grown on a wurtzite-GaAs substrate with $(1\bar{1}00)$ facets, as shown in Fig. 1, the substrate imposes additional external strains. We therefore also consider typical experimental values $\epsilon_{aa} = -0.60\%$ and $\epsilon_{bb} = -0.91\%$ [17] for the nearly external biaxial strain imposed by the substrate as measured for QW systems with $\text{Si}_{0.20}\text{Ge}_{0.80}$ barriers grown on GaAs nanowires. In addition, we study a nearly hydrostatic external strain with similar values of the in-plane deformation tensor as in the biaxial case but we also fix an external strain in growth direction with $\epsilon_{cc} = -0.66\%$, instead of allowing free relaxation along $[1\bar{1}00]$.

2. Band structures

The band structures of the defined superlattices with varying 2H-Ge QW thickness and fixed 2H- $\text{Si}_{0.25}\text{Ge}_{0.75}$ barriers, obtained with the MBJLDA XC functional, are displayed for the case of pseudomorphic growth (a) and for the case of additional external strain, here the nearly biaxial one by the substrate (b) and hydrostatic compressive strain (c), in Fig. 2. We show for comparison the projected bulk band structures of the strained barrier material as a gray background. The alignment of the band structures of the superlattice and the strained bulk alloy was performed using the branch point energies (BPEs) as reference levels. The validity of this procedure was already proven in Ref. [21] for heterostructures with interfaces parallel to the c plane. As in Ref. [21], the BPEs were computed following the method of Schleife *et al.* [36].

The superlattice bands around $\bar{\Gamma}$, close to the fundamental gap of the projected barrier band structure, describe states localized in the 2H-Ge QWs and, therefore, can be interpreted as electron and hole subbands. Qualitatively, we see that there is at least one subband below the barrier and its dispersion is similar to the one reported for the QWs of the same material with $[0001]$ orientation [21]. The lowest electron subband exhibits a parabolic behavior in a wide range of the BZ up to $0.25\bar{\Gamma M}$ and $0.35\bar{\Gamma X}$. In contrast, the highest hole subband shows a strong dispersion with a small effective mass only in a very narrow region around $\bar{\Gamma}$, while in a wider range of $\bar{\Gamma M}$ or

$\bar{\Gamma X}$ the effective hole mass increases together with a flattening of the subband. The relation of high-symmetry points in the interface BZ to such points in the bulk BZ is illustrated in Fig. SM2(b) of the Supplemental Material [35].

The evolution of the band structures with the QW thickness is observable in Fig. 2 for the cases of absence [upper panels (a)] and presence [lower panels (b) and (c)] of the external strain imposed by the substrate. The energy positions of the electron and hole subbands at $\bar{\Gamma}$ and, in particular, their difference determine the fundamental gap for electron-hole pair excitations in the 2H-Ge QW [cf. Fig. 2(e)]. The corresponding band edges of the projected barrier band structure (gray background), on the other hand, define the height of the energy barriers for electrons and holes. The *ab initio* energy band parameters at $\bar{\Gamma}$ are listed in Table I. Using this information, in the following we build a simple QW model based on the rectangular well potential [37,38].

The dispersion of the lowest electron and highest hole subband near the $\bar{\Gamma}$ point in Fig. 2 can be described by the corresponding electron (m_e^*) and hole (m_h^*) effective mass in high-symmetry directions in the 2D BZ. Such masses are listed in Table SM1 of the Supplemental Material [35] derived within two different procedures [39]. They slightly depend on the QW thickness but in a nonuniform way. One reason is related to the fact that different bulk high-symmetry points, e.g., the $\bar{\Gamma M}$ line, are projected onto the $\bar{\Gamma}$ point of the 2D BZ and $\bar{\Gamma M}$ and $\bar{MK}$ lines, as well as $\bar{\Gamma K}$ ones, are projected onto the $\bar{\Gamma X}$ line in the 2D case. The $\bar{\Gamma M}$ line is more related to the projection of the $\bar{\Gamma H}$ one in the bulk BZ. These facts are clearly illustrated in Fig. SM2(b) of the Supplemental Material [35]. The absolute values of the carrier effective masses m_e^* and m_h^* for the particles in the Ge QWs along $\bar{\Gamma M}$ and $\bar{\Gamma X}$ directions are close to the values computed for the unstrained bulk Ge lonsdaleite, with the effective electron mass $m_e^* = 0.089m$ and heavy-hole mass $m_h^* = 0.074m$ in the $\bar{\Gamma M}$ direction [27]. The thickness dependence of these masses is rather weak. There is a minor variation with the residual strain, which however is already visible from the correspondingly strained bulk 2H-Ge (see also Table SM1 of the Supplemental Material [35]). Strong increases are observed for both the electron and hole effective masses in $\bar{\Gamma X'}$ direction, the direction parallel to the c axis $[0001]$, which corresponds to the $\bar{\Gamma A}$ line in the bulk BZ. The masses reach the order of magnitude of the electron and heavy hole values, computed and measured, of about $m_e^* \approx 1.6\text{--}1.7m$ and $m_h^* \approx 0.2\text{--}0.4m$, respectively (cf. collection in Ref. [27]), along the cubic $[111]$ direction at the L point in the fcc BZ. Much closer are the electron and hole masses in the QWs to the mass values $m_e^* = 1.09m$ and $m_h^* = 0.53m$ computed for the band extrema at $\bar{\Gamma}$ in the $\bar{\Gamma A}$ direction in the BZ of 2H-Ge [27]. The latter masses are in qualitative agreement with the values listed in Table SM1 of the Supplemental Material [35] for 2H-Ge represented in large slabs with $[1\bar{1}00]$ orientation. Besides the weak confinement effect also the influence of the external strain remains small.

The confinement of both electrons and holes can be demonstrated by plotting the modulus square of the Bloch wave functions at $\bar{\Gamma}$ for the lowest empty and highest occupied states. As an example, we show in Fig. 3 such an illustration for the multi-QW structure with a well width of 8 nm and zero external strain. The probability to find an electron or

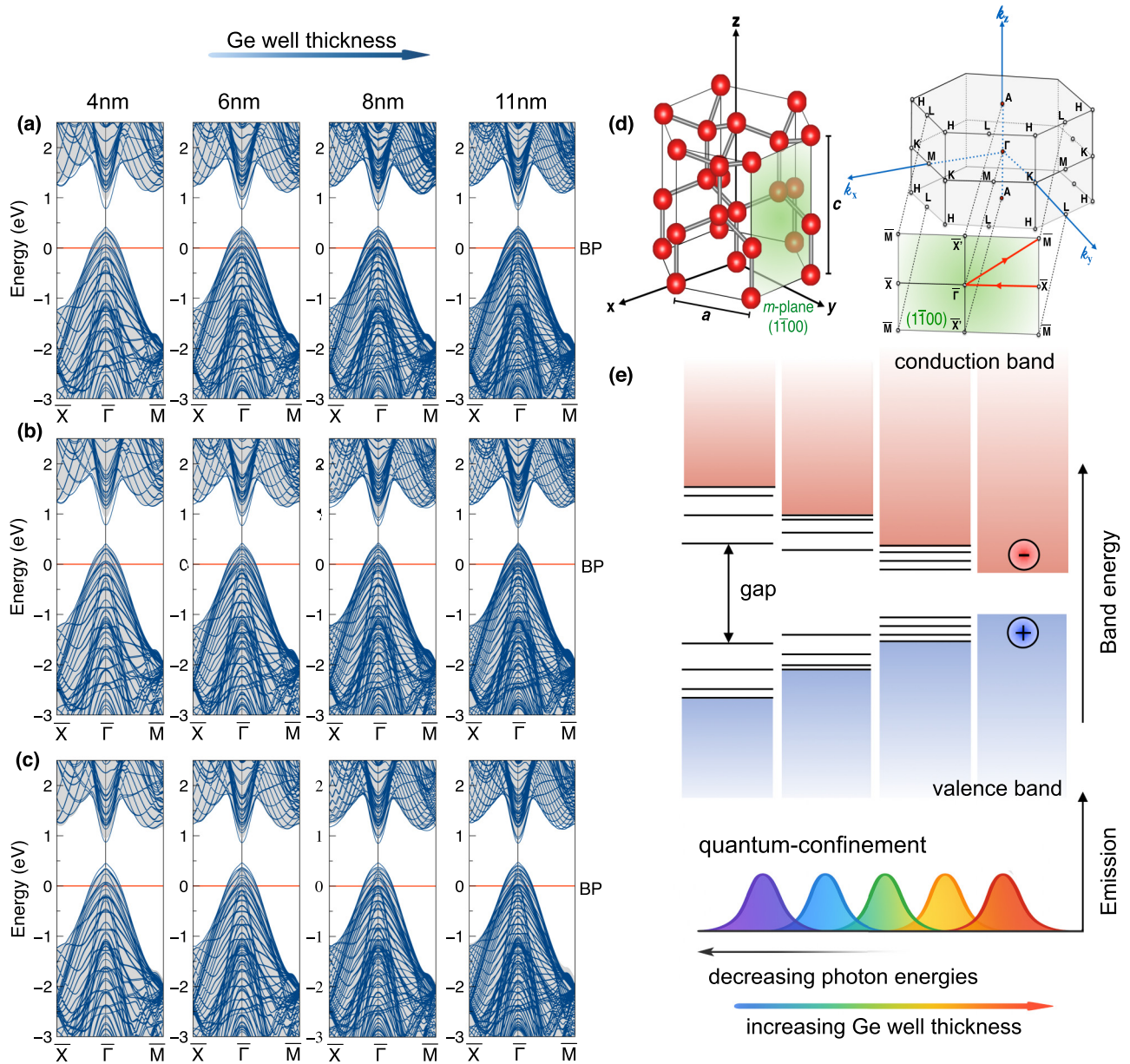


FIG. 2. Band structures of 2H-Ge/2H-Si_{0.25}Ge_{0.75} multi-QW structures (blue lines) with constant barrier thickness of $L_{\text{SiGe}} = 2$ nm and varying 2H-Ge QW thickness. The upper left panels (a) show calculated results without external strain, while the lower panels (b) and (c) represent results under external strain, biaxial and hydrostatic, respectively. The gray background illustrates the projected bulk band structure of the correspondingly strained 2H-Si_{0.25}Ge_{0.75} material [either with only internal in (a) or with also external strain in (b) and (c)]. The superlattice band structure and the projected bulk band structure are aligned using the BP (horizontal red line) as energy zero. The bands in the fundamental gap, embedded by the projected bulk conduction and valence bands, represent electron or hole subbands with wave functions localized in the 2H-Ge QWs. (d) Bulk hexagonal Brillouin zone (BZ) and its projection onto the two-dimensional BZ of the [1100] interface together with the illustration of the high-symmetry *m* plane (green shaded area) of the lonsdaleite crystal structure are also displayed to illustrate the relation of the chosen wave-vector path in 2D BZ to the projection of the bulk BZ. (e) Quantum confinement effect: a comparison between barrier band edges and QW levels, highlighting the dependence of the band gap on well thickness in QWs and the emergence of discrete energy levels near the band edges.

hole has its maximum in the center of the 2H-Ge layer of the QW. Its envelope decreases toward the interfaces to the barrier material and vanishes exponentially into the 2H-Si_{0.25}Ge_{0.75} barriers. The envelopes of the two probability densities show the behavior expected for carriers in a rectangular QW with finite barriers [38]. In Figs. 3(a) and 3(b) not only the envelope character of the Bloch functions is visible but also their atomic

origin. The hole wave function consists of bonding combinations of almost sp^3 hybridized orbitals along the chemical bonds with a directional component parallel to the (1100) interface. In the case of the electron wave function the atomic contributions look similar to localized *p* orbitals forming anti-bonding combinations. Higher electron or hole subbands can be hardly seen from the band structure in Fig. 3(b). However,

TABLE I. Energy parameters (in eV) at $\bar{\Gamma}$ taken from Fig. 2 for heterostructures with a varying QW thickness up to $L_{\text{Ge}} = 15$ nm and 2-nm-wide barriers. The multi-QW systems are relaxed without and with additional biaxial or hydrostatic strain imposed by the substrate (see text). Results for the three (zero, compressive biaxial, compressive hydrostatic) strains are displayed in corresponding rows on top of each other. The valence and conduction band energies E_v and E_c are given with respect to the corresponding BPE. In addition, the resulting energy gaps E_g , as well as the electron ionization energy I_e and hole ionization energy I_h , are listed. The larger barrier gaps $E_g = 0.56\text{--}0.59$ eV, increased with respect to the unstrained 2H-Si_{0.25}Ge_{0.75} bulk [12,21], go back to the inclusion of strain due to pseudomorphic growth on strained or unstrained 2H-Ge well material and the shift of the p -like conduction band away from the p -derived valence band top under tensile strain.

QW thickness	Ge QW			SiGe barrier			I_h	I_e
	E_v	E_c	E_g	E_v	E_c	E_g		
4 nm	0.417	0.783	0.366	0.377	0.953	0.576	0.040	0.170
	0.407	0.779	0.372	0.368	0.933	0.565	0.039	0.154
	0.452	0.872	0.420	0.361	0.952	0.591	0.091	0.080
6 nm	0.426	0.768	0.342	0.377	0.953	0.576	0.049	0.185
	0.418	0.767	0.349	0.371	0.939	0.568	0.047	0.172
	0.459	0.859	0.400	0.361	0.951	0.590	0.098	0.092
8 nm	0.431	0.749	0.318	0.378	0.954	0.576	0.053	0.205
	0.423	0.759	0.336	0.365	0.929	0.568	0.058	0.174
	0.461	0.846	0.385	0.361	0.951	0.590	0.100	0.105
11 nm	0.435	0.745	0.310	0.377	0.953	0.576	0.058	0.208
	0.425	0.744	0.319	0.368	0.933	0.565	0.057	0.189
	0.471	0.841	0.370	0.361	0.951	0.590	0.110	0.110
15 nm	0.437	0.740	0.303	0.377	0.953	0.576	0.060	0.213
	0.426	0.728	0.302	0.368	0.933	0.565	0.058	0.205
	0.480	0.831	0.351	0.361	0.951	0.590	0.119	0.120

investigations of the wave function localization as shown in Fig. 3 may be helpful to identify more subbands. We did this test for the quantum well of Fig. 3. Indeed, the wave functions of the second electron and second hole subbands of the 8 nm Ge/2 nm Si_{0.25}Ge_{0.75} multi-QW structure also exhibit a clear quantization in the 2H-Ge layer.

3. Confinement and quantization

The general trends of the band gaps as a function of the well thickness can be read from Table I. Carriers confined in the 2H-Ge wells experience band gaps that decrease from a value of $E_g = 0.37$ eV (0.42 eV with the additional compressive hydrostaticlike strain) for $L_{\text{Ge}} = 4$ nm to 0.30 eV (0.30 or 0.35 eV with the additional external strain) for $L_{\text{Ge}} = 15$ nm. We recall that the theoretical bulk band gap for unstrained 2H-Ge is about 0.30 eV [12,15,21]. The corresponding values for the 2H-Si_{0.25}Ge_{0.75} alloy barrier are 0.57 eV (0.56 or 0.59 eV with external strain) and remain almost constant irrespective of the QW thickness.

The trends of the fundamental gaps in the QWs clearly show a decrease with increasing QW thickness L_{Ge} , as it can be expected as a consequence of the decreasing quantum confinement. The variation of the 2H-Si_{0.25}Ge_{0.75} gaps with the thickness of the 2H-Ge QW wells is very weak, whereas their absolute values are also increased because of the p -like character of both band edges, in contrast to the expectation for sp gaps. The trends of the gaps versus QW thickness are confirmed by the values of the ionization energies of electrons I_e and holes I_h , defining the energy distance of the lowest electron and highest hole subband to the projected barrier band structure at $\bar{\Gamma}$. They describe the energy to transfer an electron and hole, respectively, from the lowest state in the

QW into the barrier material. The ionization energies increase with increasing thickness, indicating the reduced effect of the carrier confinement. While the biaxial strain influence on I_h and I_e is relatively weak, a strong variation happens for hydrostatic strain.

The band edges E_c and E_v at $\bar{\Gamma}$ and the fundamental QW gaps E_g are displayed in Fig. 4 versus the thickness L_{Ge} of the 2H-Ge QW. The values for E_c and E_v in Fig. 4(a) are given with respect to the BPE [36] of the QW or barrier material. The resulting fundamental gaps inside the 2H-Ge QWs are compared in Fig. 4(b) with experimental values [17]. All parameters are extracted from the band structures in Fig. 2 and especially the band parameters listed in Table I.

The strong dependence on the thickness L_{Ge} of the 2H-Ge layer on the QW energies is visible in both subfigures of Fig. 4 (the corresponding values are listed in Table I). In Fig. 4(a) we observe that the band edges E_c and E_v of the Si_{0.25}Ge_{0.75} barrier material also show an almost vanishing influence of thickness on the band positions, converging toward fixed values for a given external strain due to the almost complete accommodation of the lattice mismatch in the thinner barrier material if combined with wide wells. These shifts of the band positions, together with a gap opening for small 2H-Ge thickness, represent the trend to an almost symmetric distribution of compressive strain in Ge QW layers and tensile strain in the barrier layers for thin 2H-Ge layers [21]. The additional external strains act in a different way. Whereas the biaxial strain has only a minor influence, the nearly hydrostatic strain shifts the band edges to somewhat higher (E_c) or lower (E_v) energies. The variation of the band edges around the fundamental gaps of the superlattices are, however, mainly a consequence of the decreasing confinement of the electron and hole wave functions with increasing thickness L_{Ge} of the

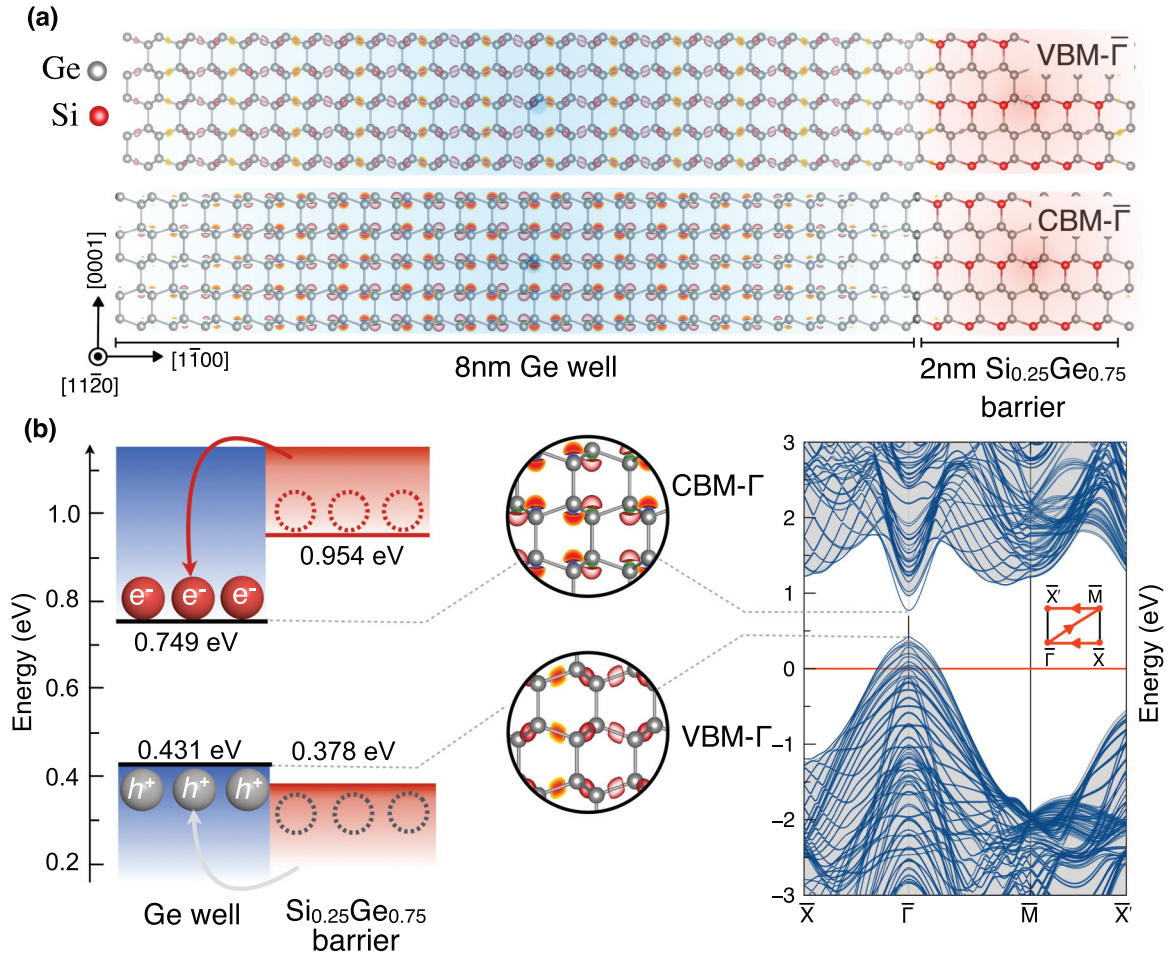


FIG. 3. (a) Squared modulus of the wave functions of the lowest electron and highest hole subband states at $\bar{\Gamma}$ for the multi-QW structure with a 2H-Ge layer of 8 nm and a barrier of 2 nm, in the case of internal strain only. The positions of the Ge atoms (gray circle) and Si atoms (red circle) are shown from a side view. Bloch functions are visible along with their atomic origin. The hole wave function consists of bonding combinations of almost sp^3 hybridized orbitals along the chemical bonds with a directional component parallel to the $(1\bar{1}00)$ interface. In the case of the electron wave function the atomic contributions look similar to localized p orbitals forming antibonding combinations. (b) Band structure of multi-QW structure of the correspondingly unstrained 2H-Ge/2H-Si_{0.25}Ge_{0.75} shown in (a). In the right panel the gray background illustrates the projected bulk band structure of 2H-Si_{0.25}Ge_{0.75}. The BP energy (horizontal red line) is used for alignment. A zoom in the band structure onto a small energy region around the fundamental gap and around the $\bar{\Gamma}$ point in reciprocal space are displayed in the left panel. The lowest conduction and highest valence band edges are shown schematically in the left panel. The QW subband levels in the confined Ge layer and the corresponding band edges of bulk strained 2H-Si_{0.25}Ge_{0.75} are displayed for comparison. The zooms of the wave function of the lowest electron and the highest hole band in the 2H-Ge region are presented to illustrate the most important subband states (middle panel).

2H-Ge QW layers. The absolute energy positions of all band edges in the multi-QW structures as well as in the bulk barrier systems are strongly determined by the applied external strain, zero or $\epsilon_{aa} = -0.0060$, $\epsilon_{bb} = -0.0091$, or in addition $\epsilon_{cc} = -0.0060$.

The combined confinement effects are illustrated for the fundamental band gaps of the multi-QW structures and, equivalently, for the isolated 2H-Ge QWs in Fig. 4(b). The carrier confinement vanishes with rising QW thickness $L_{\text{Ge}} \rightarrow \infty$. Consequently, the actual gaps approach the gap values of unstrained and strained 2H-Ge, 0.30 eV (no external strain and biaxial one), 0.25 eV (for compressive biaxial strain), and 0.33 eV (with external hydrostaticlike strain), respectively. The absolute experimental gap values shown for comparison in Fig. 4(b) are extracted from PL measurements [17] and correspond to the onset values of the emission spectra. They

exhibit the same dependence on L_{Ge} as the theoretical gap curve in the strained case. The absolute values of the estimated experimental band gaps are only slightly larger than the calculated values, as a consequence of their determination from the onset of the emission spectra. In the hydrostatic strain case the average discrepancy amounts to only 60 meV.

4. Model of rectangular quantum wells

The thickness dependence on L_{Ge} illustrated in Figs. 2 and 4 for the approximate QP band structures and energy band extrema at $\bar{\Gamma}$ can be explained in a simplified picture due to the combined effects of electron and hole quantum confinement, modified by the mutual strain of well and barrier layers, weighted by their thicknesses L_{Ge} and $L_{\text{SiGe}} = 2$ nm, and when it is the case by additional external biaxial or hydrostatic strain exerted by the substrate.

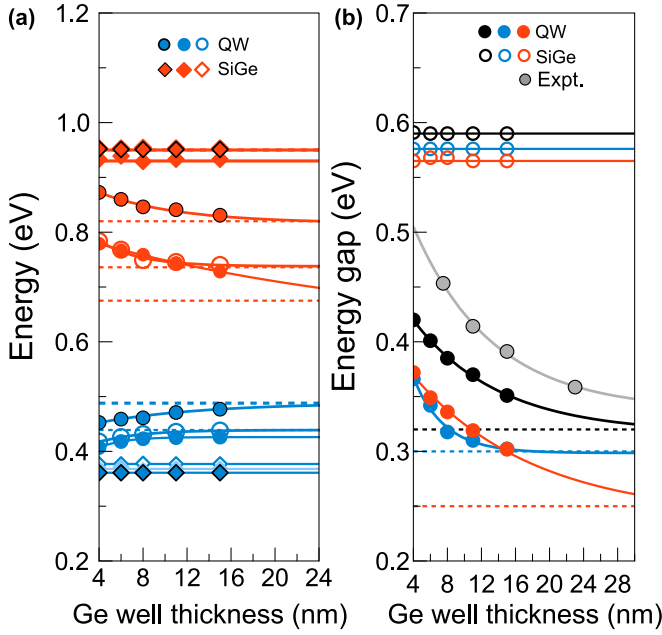


FIG. 4. (a) Conduction E_c (in red) and valence E_v (in blue) band edges at $\Gammā$, as well as (b) band gaps E_g for the unstrained (blue circle) or strained (red circle for compressive biaxial strain and black circle for compressive hydrostatic strain) multi-QW structures versus thickness L_{Ge} of the 2H-Ge QW. The band positions in (a) are displayed with respect to the corresponding BPE. (a) In addition, the band edges of unstrained/strained bulk barrier materials are displayed, all aligned with respect to their BPE. (b) The calculated band gaps in the QWs are compared with experimental values of strained systems estimated from PL measurements [17]. The additional horizontal dashed lines extrapolate the band gap energies at large QW thickness (bulk limit).

To model the effect of quantum confinement alone we construct a model consisting of finite rectangular QWs [37,38]: both electrons and holes are confined in the Ge layer by the presence of SiGe barriers [cf. Fig. 5(a)]. The corresponding QW parameters in Table I are extracted from *ab initio* band structures such as those given in Fig. 2. The QWs are characterized by their width L_{Ge} and the potential barriers ΔE_c and ΔE_v , the band offsets. The band discontinuities are obtained by the calculation of the band edges E_c and E_v of the strained bulk 2H-Ge and the strained bulk 2H-Si_{0.25}Ge_{0.75} barrier material aligned using the BPEs [36]. Therefore, the offsets are significantly influenced by the actual strain stage in the well and barrier materials but also especially their ratio, the chosen method of BPE calculation.

The calculated band offsets are plotted in Figs. 5(b) and 5(c) (including an external strain produced by the substrate) and 5(d) (without external strain). The corresponding values are also listed in Table II. The distances between the bottoms of the rectangular wells for electrons and holes in the bulk strained 2H-Ge layers correspond to the band gaps E_g^{2H-Ge} , while the distance between the two barriers in the 2H-SiGe layers is given by the band gap $E_g^{2H-SiGe}$. The quasiparticle gap E_g of electron-hole excitations inside the well region is modified by the sum $\varepsilon_e + \varepsilon_h$ of the confinement energies to $E_g = E_g^{2H-Ge} + \varepsilon_e + \varepsilon_h$.

TABLE II. Band offsets ΔE_v and ΔE_c and confinement energies ε_h , ε_e , and $\varepsilon_e + \varepsilon_h$ for the three (zero, compressive biaxial, and compressive hydrostatic) strains given in lines on top of each other. All values are extracted from approximate QP band structures and their BPE alignment.

QW thickness L_{Ge}	Band offsets		Confinement energies		
	ΔE_v	ΔE_c	ε_h	ε_e	$\varepsilon_e + \varepsilon_h$
4 nm	0.062	0.215	0.022	0.045	0.067
	0.059	0.260	0.020	0.106	0.126
	0.127	0.152	0.036	0.072	0.108
6 nm	0.062	0.215	0.013	0.030	0.043
	0.056	0.266	0.009	0.094	0.103
	0.127	0.151	0.029	0.059	0.088
8 nm	0.061	0.216	0.008	0.011	0.019
	0.062	0.260	0.004	0.086	0.090
	0.127	0.151	0.027	0.046	0.073
11 nm	0.062	0.215	0.004	0.007	0.011
	0.059	0.260	0.002	0.071	0.073
	0.127	0.151	0.017	0.041	0.058
15 nm	0.062	0.215	0.002	0.002	0.004
	0.059	0.260	0.001	0.055	0.056
	0.127	0.151	0.008	0.031	0.039

The confinement energies ε_e and ε_h , whose values are given in Table II, are plotted in Figs. 5(e)–5(g). These values were extracted from Figs. 2(a), 2(b), and 2(c), combined with the computations of the band structures of bulk strained 2H-Ge, or more precisely of their band edges E_c and E_v given in Table I. The confinement energies are calculated as $\varepsilon_e = E_c(\text{multi-QW}) - E_c(\text{bulk-Ge})$ and $\varepsilon_h = E_v(\text{bulk-Ge}) - E_v(\text{multi-QW})$, after performing the described BPE alignment. Together with E_g^{2H-Ge} , the sum $\varepsilon_e + \varepsilon_h$ [also in Figs. 5(e), 5(f), and 5(g)] delivers the fundamental gap E_g of the multi-QW structures displayed in Fig. 2 and Fig. 4(b). Whereas the individual confinement energies ε_e and ε_h depend on the actual BPE value and, in general, on the alignment procedure, their sums do not. Ionization energies and confinement energies are related to the band discontinuities via $\Delta E_c = I_e + \varepsilon_e$ and $\Delta E_v = I_h + \varepsilon_h$.

The band discontinuities ΔE_c and ΔE_v , the depths of the QWs, in Figs. 5(b)–5(d) (cf. Table II for the precise values) vary only weakly with the 2H-Ge QW thickness. They display a pronounced dependence on the applied external strain, while their sums $\Delta E_c + \Delta E_v$ are 0.28 (0.32, 0.28) eV for zero (biaxial, hydrostatic) external strain and are also less influenced by strain. The individual band offsets however vary in the interval 0.06–0.26 eV. The biaxial strain exhibits only a small influence by minor increase of ΔE_c and, hence, increases the electron confinement. More drastic is the influence of the nearly hydrostatic strain. The electron QW depths are flattened, while the hole barriers are significantly increased. These offset values are comparable with the values calculated for the QWs with [0001] orientation [21,22]. The minor thickness dependence of the band offsets in Figs. 5(b)–5(d) is a consequence of the interface strain because of the assumed pseudomorphic growth. However, the variation of ΔE_v and ΔE_c versus L_{Ge} remains small compared to their absolute values.

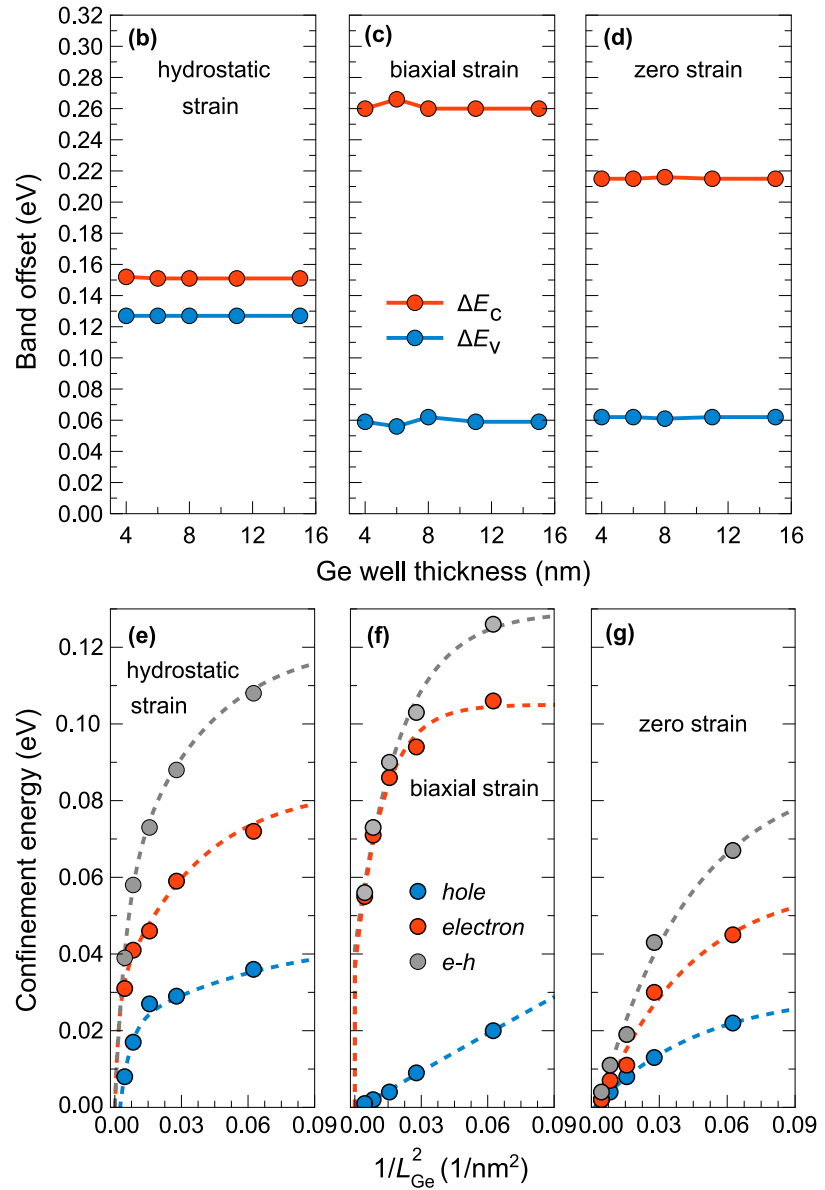


FIG. 5. (a) Illustration of the rectangular quantum well model for electrons and holes. The band gaps $E_g^{2\text{H-Ge}}$ and $E_g^{2\text{H-SiGe}}$ of the bulk well and barrier materials are also shown. The resulting alignment corresponds to a type-I heterostructure, where both electrons and holes are confined in the same layer (2H-Ge). (b)–(d) Dependence of the conduction and valence band discontinuities ΔE_c and ΔE_v on the QW thickness L_{Ge} . (e)–(g) Resulting confinement energies ε_e , ε_h , and $\varepsilon_e + \varepsilon_h$ as a function of $1/L_{\text{Ge}}^2$.

The confinement energies ε_e , ε_h , and $\varepsilon_e + \varepsilon_h$ plotted in Figs. 5(e), 5(f), and 5(g) versus the inverse square $1/L_{\text{Ge}}^2$ of the QW thickness, and also listed in Table II, vanish for extremely large well thicknesses as expected. When the well thickness L_{Ge} gets very small, they tend to values that remain smaller than the barrier heights (i.e., the band offsets ΔE_c and ΔE_v). Indeed, it holds that $\varepsilon_{e/h} < \Delta E_{c/v}$, as expected from the fact that there is always at least one confined state in a finite rectangular quantum well. The absolute values of the electron confinement energies ε_e are for the majority of well thicknesses, even for larger well thicknesses of the order of or bigger than $k_B T = 25$ meV, the thermal energy at room temperature. Therefore, confinement effects of electrons should be observable in a wide temperature range. In general, the confinement effect on holes is weaker but should still

play a role in the low-temperature range. In optical absorption or emission, which are ruled by intersubband transitions, Figs. 5(e), 5(f), and 5(g) indicate that confinement effects should be visible in QWs up to thicknesses of 10 nm. Only without external strain and larger thicknesses should the temperature be reduced in measurements.

For deep wells the confinement energies may be approximated by $\varepsilon_{e/h} = \pi^2 \hbar^2 / (L_{\text{Ge}}^2 2m_{e/h}^*)$ [37,38], that is the analytic formula for the case of infinite barriers, using the effective-mass approximation (EMA) with the electron and hole masses m_e^* or m_h^* along the $[1\bar{1}00]$ direction. Indeed, for small values of $1/L_{\text{Ge}}^2$ the confinement energies, especially those of the holes, in Figs. 5(e)–5(g) exhibit an almost linear behavior independent of strain. For an estimate of the effective carrier masses $m_{e/h}^*$ in confinement direction $[1\bar{1}00]$ we apply

the model of a finite rectangular well with barrier height $\Delta E_{c/v}$. Then, the effective masses of particles-in-box follow directly from the *ab initio* values of the confinement energy $\varepsilon_{e/h}$ [38] as $m_{e/h}^* = \frac{\hbar^2}{2L_{Ge}^2 \varepsilon_{e/h}} (2 \arctan \sqrt{\frac{\Delta E_{c/v} - \varepsilon_{e/h}}{\varepsilon_{e/h}}})^2$, if the deviation of the effective masses in well and barrier regions are neglected and the rectangular wells form a reliable model. The effective masses in $[1\bar{1}00]$ direction that we can extract vary around the averaged values $m_e^* \approx 0.39(0.03, 0.05)m$ and $m_h^* \approx 0.48(0.94, 0.16)m$ for the case without (with) external (biaxial, hydrostatic) strain. All values derived for a given QW thickness L_{Ge} and band offset $\Delta E_{c/v}$ are also listed in Table SM1 of the Supplemental Material [35] together with the effective masses in perpendicular directions found from the subband dispersion. In general, the particle-in-the-box masses significantly deviate from the effective masses computed for carriers moving along $[1\bar{1}00]$ in the unstrained 2H-Ge bulk. The values determined from the confinement without external strain are somewhat larger than the electron and heavy hole masses calculated for bulk 2H-Ge in the ΓM direction perpendicular to the c axis, $m_e^* = 0.052m$ and $m_h^* = 0.089m$ [27]. It seems that the quantization in the wells makes both carriers, especially the holes, heavier compared to the bulk case. Thereby, a significant influence of the external strain is observed, making generally the electron masses smaller while the hole mass is increased (biaxial case) or decreased (hydrostatic case) (cf. Table SM1 of the Supplemental Material [35]). Nevertheless, the relation $m_e^* < m_h^*$ is still valid, independent of strain and confinement. They significantly vary with the QW thickness with or without external strain. The infinite well model is hardly valid, also not for large QW thicknesses. The finite well model is applicable, but with substantially modified carrier masses compared to the bulk results.

The *ab initio* band structures in Fig. 2 also allow the discussion of the subbands appearing for a given QW thickness L_{Ge} and their influence on optical emission spectra. The characteristic intersubband energies $\Delta \varepsilon_n$ for optical transitions at $\bar{\Gamma}$ from a hole subband v_n into an electron subband c_n ($n = 1, 2, \dots$) are listed in Table SM2 of the Supplemental Material [35]. In this table also the strengths of the intersubband transitions are characterized by the squares of the dipole matrix elements $(ex_n)^2$ and $(ez_n)^2$ with the expectation values $x_n = \langle c_n | x | v_n \rangle$ and $z_n = \langle c_n | z | v_n \rangle$ for light polarization in the x direction $[11\bar{2}0]$ and z direction $[1\bar{1}00]$, respectively. The values $(ey_n)^2$ with $y \parallel [0001]$ almost vanish and, therefore, are not displayed. This observation is more or less in agreement with the group-theory findings for the optical transition $\Gamma_9^+ \rightarrow \Gamma_8^-$ from the valence-band top into the lowest minimum of the conduction bands at Γ in lonsdaleite and wurtzite crystals for light polarization parallel to the c axis [14,27]. From Table SM2 of the Supplemental Material [35] one reads the existence of an increasing number of subbands in the electron and hole QW, from only the $n = 1$ subbands in the narrow QW of $L_{Ge} = 4$ nm to three subbands $n = 1, 2$, and 3 in the QW with $L_{Ge} = 15$ nm, independent of the presence of the external strain. Because of the finiteness of the electron and hole QW depths the n^2 law is violated for the subband energies, again illustrating the limited application of the rectangular well model. Only in the 6 nm QW without external strain does the subband energy difference between

$n = 1$ and $n = 2$ of 172 meV agree with the value $(4\varepsilon_e + \varepsilon_h)$ from Table II.

The optical dipole matrix elements are also listed in Table SM2 of the Supplemental Material [35] for different light polarizations $x \parallel [11\bar{2}0]$ and for $z \parallel [1\bar{1}00]$. For these light polarizations perpendicular to the c axis, which lie in the m -plane interface, the matrix elements remain small, somewhat below the values for allowed transitions in the barrier region [14]. Thereby the matrix elements parallel to the x axis and for the $n = 1$ transitions are the larger ones, independent of the QW thickness and the external strain. The absolute values of the $n = 1$ matrix elements exhibit similar values as the lowest transitions in the bulk 2H-Ge, which are given in [14,27] as matrix elements of the momentum operator. This can be clearly seen applying the relation $p_{jn}^2 = (\frac{m}{\hbar} \Delta \varepsilon_n)^2 (ex_j)^2$ with $j = x, z, n = 1, 2, 3, \dots$ and $\Delta \varepsilon_n$ as the corresponding intersubband energy [40] for the matrix elements of the momentum operator. The analysis above fully validates the qualitative use of a rectangular quantum well model with finite barriers [cf. Fig. 5(a)] and appropriate effective electron and hole masses along $[1\bar{1}00]$. This model can be, e.g., used to support the interpretation of experiments of light emission in hexagonal SiGe heterostructures. Of course, qualitative deviations from the estimates within the effective-mass approximation and the rectangular well model need to be acknowledged. The exact energy and oscillator strength values should be taken from the *ab initio* calculations including the quasiparticle effects.

B. Other interface orientations

1. $(11\bar{2}0)$ a -plane interfaces

To model QW structures with an interface perpendicular to the direction $[11\bar{2}0]$ without external strain, we built orthorhombic supercells comprising 224 atoms (56 atomic layers). Each layer contained four atoms in the 2D lateral unit cell (as depicted in Fig. SM2 of the Supplemental Material [35]), with a nominal thickness of about $a/2$ or a bilayer with a nominal thickness of a and eight atoms in a 2D unit cell. The crystal axes were denoted as $\mathbf{a}_a, \mathbf{b}_a$, and $\mathbf{c}_a$. We assumed an ordered arrangement of Si atoms in the 2H-Si_{0.25}Ge_{0.75} barrier materials, ensuring that in each 2D unit cell and atomic layer, one Si atom appeared. Nominal relationships were maintained, i.e., $a_a = c$, $b_a = \sqrt{3}a$, and $c_a = 28a$, although lattice parameters a and c varied with composition and internal strain for the 2H systems. After the atomic relaxation of the superlattice, three systems with (1) 11 SiGe-alloy layers and 45 Ge layers, (2) 28 SiGe layers and 28 Ge layers, and (3) 56 SiGe layers and no Ge layers exhibited orthorhombic lattice parameters $a_a = 6.5671$ (6.5464, 6.5178) Å, $b_a = 6.8870$ (6.8669, 6.8351) Å, and $c_a = 111.3665$ (110.9948, 110.4927) Å. Corresponding values for pure unstrained 2H-Ge were $a_a = 6.5920$ Å, $b_a = 6.9213$ Å, and $c_a = 111.8880$ Å.

At the pseudomorphic interface between 2H-Ge and 2H-Si_{0.25}Ge_{0.75} a macroscopically compressive (on 2H-Ge) and tensile (on the SiGe alloy) biaxial strain is generated due to their different lattice parameters. These strains have effects that are accordingly weighted by the layer thicknesses $L_{Ge} = 9.1$ (5.5, 0.0) nm and $L_{SiGe} = 2.0$ (5.5, 11.0) nm [21]

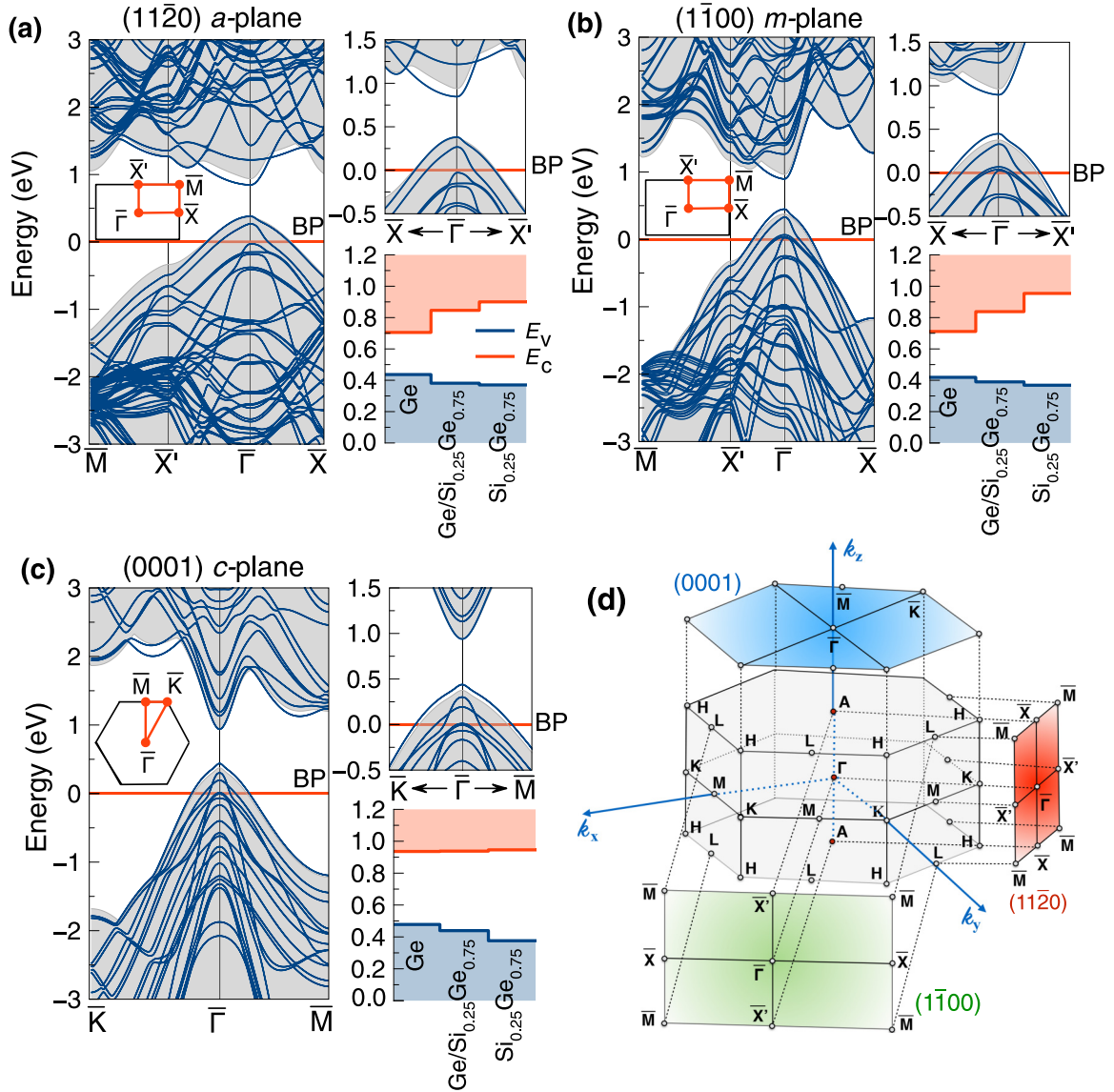


FIG. 6. Superlattice band structures (large left panel) together with the projected band structure of the bulk strained $\text{Si}_{0.25}\text{Ge}_{0.75}$ layers (gray shaded areas) for multi-QWs with nearly the same well and barrier thicknesses $L_{\text{Ge}} \approx L_{\text{SiGe}}$, but different interface orientations: (a) $[11\bar{2}0]$, (b) $[1\bar{1}00]$, and (c) $[0001]$. The actual thicknesses are $L_{\text{Ge}} = 1.3$ nm (a), 1.6 nm (b), 1.6 nm (c) and $L_{\text{SiGe}} = 1.1$ nm (a), 1.1 nm (b), 1.1 nm (c). The BP energies (horizontal red lines) are used for alignment. The zooms in these band structures onto a small energy region around the fundamental gap and around the $\bar{\Gamma}$ point in reciprocal space are displayed in the small upper-right panels. The lowest conduction (E_c) and highest valence (E_v) band edges are shown schematically in the small lower-right panels. The QW subband levels in the confined Ge layers and the corresponding band edges of bulk strained 2H- $\text{Si}_{0.25}\text{Ge}_{0.75}$ are displayed for comparison. The characteristic confinement energies ε_e of electrons and ε_h of holes as well as the ionization energies I_e and I_h are clearly visible. (d) Bulk hexagonal BZ and its projections onto the two-dimensional BZs of the m -, a -, and c -plane interfaces. While high-symmetry points of the bulk BZ are denoted with Γ , M , K , ..., such points in the 2D BZs are indicated by modified denotations $\bar{\Gamma}$, $\bar{X}$, $\bar{M}$.

in situations (1) [(2), (3)]. The values of the resulting biaxial strains varied between $\epsilon_{aa} = -0.69\%$ (0.43%) and $\epsilon_{bb} = -0.50\%$ (0.46)% for 2H-Ge (SiGe alloy) for nearly equal thicknesses $L_{\text{Ge}} = L_{\text{SiGe}}$, and $\epsilon_{aa} = 0\%$ (1.13%) and $\epsilon_{bb} = 0\%$ (1.25)% for 2H-Ge (SiGe alloy) for thick QWs with $L_{\text{Ge}} \gg L_{\text{SiGe}}$. While the order of magnitude of the resulting strain was consistent with the results for interface orientation in the m plane ($1\bar{1}00$), the exact values are different. Considering typical values for the deformation potentials for electron and hole states, found for the $[0001]$ orientation in Ref. [21], significant shifts of the band energies with varying QW thickness

L_{Ge} were anticipated for the $[11\bar{2}0]$ orientation, akin to those observed in Sec. III A for $(1\bar{1}00)$ interfaces.

2. Subbands and quantization

Due to the anticipated similar strain effects for the $[11\bar{2}0]$ orientation, our focus is on the case of vanishing external strain for a superlattice with nearly equal thicknesses $L_{\text{Ge}} \approx L_{\text{SiGe}}$. For a geometry (2) similar to the one discussed above, involving a -plane interfaces and $L_{\text{Ge}} \approx 13.5$ nm and $L_{\text{SiGe}} \approx 10.5$ nm, the superlattice band structure is presented in Fig. 6(a), together with the projected bulk strained band

structure of the barrier material. A zoom into the essential energy bands around the fundamental gap and the $\bar{\Gamma}$ point is also provided. The relation of interface and bulk BZs is also described in Fig. SM2(a) of the Supplemental Material [35]. Qualitatively, we observe the same behavior as previously identified in Fig. 3 for the $[1\bar{1}00]$ orientation and also for the $[0001]$ orientation, as described elsewhere [21]. Once again, at least one electron subband and one hole subband are clearly observable around $\bar{\Gamma}$. The confinement characteristics of these subband states have been studied, as illustrated in Fig. 3. Indeed, both the electron and the hole wave functions are localized in the region of the 2H-Ge QW, consistent with the findings for the m -plane QWs.

This result unmistakably characterizes the type-I nature of the 2H-Ge/2H-Si_{0.25}Ge_{0.75} ($11\bar{2}0$) multi-QW heterostructure. Despite the effects of the compressive strain in the 2H-Ge region, the wave functions of electrons and holes are localized in the well. The confinement effect is evident through the opening of the superlattice gap E_g in comparison to the gap of the strained 2H-Ge bulk, E_g^{2H-Ge} . This behavior can be qualitatively understood also within the framework of the rectangular QW model [37,38] for the motion of electrons and holes, described by the BPE-aligned positions of E_c and E_v for the compressibly strained bulk 2H-Ge, the tensilely strained bulk 2H-Si_{0.25}Ge_{0.75}, and the 2H-Ge/Si_{0.25}Ge_{0.75} ($11\bar{2}0$) superlattice. The type-I character is evident and it is apparent that electron confinement is much stronger than hole confinement, in agreement with the smaller electron effective mass [27]. The gaps are $E_g^{2H-Ge} = 0.29$ meV, $E_g^{2H-SiGe} = 0.58$ eV, and $E_g = 0.44$ eV (of the QW), the confinement energies $\varepsilon_e = 141$ meV and $\varepsilon_h = 55$ meV, the ionization energies $I_e = 54$ meV, $I_h = 11$ meV, and, consequently, band offsets $\Delta E_c = 195$ meV and $\Delta E_v = 66$ meV. These energies are comparable with the corresponding values of the $[1\bar{1}00]$ orientation in Tables I and II.

3. Orientation variation

The band behavior near the conduction and valence band edges E_c and E_v for the $[1\bar{1}00]$ interface orientation in Fig. 6(b) closely resembles the findings in Fig. 6(a) for $[11\bar{2}0]$. The confinement picture is qualitatively consistent across both subfigures (a) and (b) of Fig. 6. A distinct electron subband becomes apparent somewhere in the middle of the pronounced electron QW, as indicated in the small lower right panels. In the hole case, at least one subband also emerges in the hole well, albeit with a smaller confinement energy [$\varepsilon_h = 29$ (55) meV] and $I_h = 21$ (11) meV due to the larger hole mass and the smaller barrier height. Given that the hole mass m_h^* is generally larger than the electron mass m_e^* [27], the electron confinement energy ε_e is consistently larger than the hole energy ε_h . Consequently, the gap opening in the 2H-Ge QWs with confinement primarily arises from the quantization of electron states in the electron QW.

In contrast, the $[0001]$ interface orientation exhibits a nearly flat conduction band offset, leading to extremely weak electron confinement (2 meV) and ionization (8 meV) energies, as illustrated in Fig. 6(c). This behavior arises due to strain-induced band gap widening of 2H-Ge under compressive biaxial strain (without external strain) compared with the tensilely strained bulk 2H-Si_{0.25}Ge_{0.75} and the

2H-Ge/Si_{0.25}Ge_{0.75}(0001) superlattice. The hole confinement (39 meV) and ionization (63 meV) energies, on the other hand, remain relatively strong and consistent across all three interface orientations, indicating that the valence band alignment is less affected by orientation and local strain effect compared to the conduction band edges, as indicated in the small lower right panels. For the $[11\bar{2}0]$ and $[1\bar{1}00]$ interface orientations, compressive mutual strain however leads to a decrease in band gap of 2H-Ge with respect to 2H-Ge/Si_{0.25}Ge_{0.75} QW and the barrier materials, which increases conduction band offset and, therefore, enhances the quantum confinement of electrons, as described above. Despite qualitative agreement for differently oriented QWs, the specific values of ε_e , ε_h , and $\varepsilon_e + \varepsilon_h$ clearly depend on the orientation of the QW interfaces between 2H-Ge and 2H-Si_{0.25}Ge_{0.75}.

IV. CONCLUSIONS

The structural and electronic properties of pseudomorphically grown, hexagonal Ge/Si_{0.25}Ge_{0.75} multi-QW arrangements have been studied for varying QW thicknesses, interface orientations, and external strains by means of DFT calculations, taking approximate quasiparticle corrections to the band structures into account, using state-of-the-art exchange-correlation functionals for accurate band structures. The results, especially energy shifts and wave function localization, are discussed in terms of a rectangular-well potential model for both carrier types, electrons and holes. In general, we found a type-I heterostructure behavior, i.e., confinement of electrons and holes in the 2H-Ge regions of the multi-QW structures, independent of the actual crystallographic orientation of the QW interfaces, the QW thickness L_{Ge} , and the applied external strain. However, all these parameters influence the actual electron and hole confinement energies, as well as the modification of the fundamental gap E_g^{2H-Ge} of the 2H-Ge material due to quantum confinement and to the local strain.

In the case of $[1\bar{1}00]$ -oriented QWs with m -plane interfaces, the dependence of the QW layer thickness L_{Ge} is studied for a small fixed barrier thickness $L_{SiGe} = 2$ nm. We considered three cases: pseudomorphic growth without additional strain or including external biaxial or hydrostatic strain due to the substrate, applying experimental values in the biaxial case. In the strain-free and biaxial strain case and $[1\bar{1}00]$ orientation deeper electron wells with about $\Delta E_c = 0.22$ or 0.26 eV compared to the flat hole well with $\Delta E_v = 0.06$ eV have been observed. In the case of almost external hydrostatic strain the electron and hole offsets approach similar values 0.13 and 0.15 eV, respectively. In all situations, we observe quantization effects on both electrons and holes, i.e., a type-I behavior. More precisely, we always identify at least one electron and one hole subband with wave functions confined in the 2H-Ge QW regions. The valence band offsets vary in the range of 0.06–0.13 eV depending on strain. For the conduction bands the variation $\Delta E_c = 0.15$ –0.26 eV is bigger. In general, there is a tendency for stronger quantization of the electrons compared to the holes, consistent with the effective-mass difference. The interplay between well depth, QW width, and carrier masses allows a significant variation of the quantization energies with the QW thickness L_{Ge} . However, the $1/L_{Ge}^2$ dependence expected for deep wells and the

validity of the effective-mass approximation are only found for the QW structures with not too small QW thicknesses. This holds, in general, for electrons and holes with and without additional substrate-induced strain. The corresponding effective masses for particles-in-the-box are close to the values calculated from first principles or smaller (larger) for electrons (holes) when external strain is included.

The influence of the crystallographic orientation of the QW interfaces has been investigated for similar thicknesses of the 2H-Ge well and the Si_{0.25}Ge_{0.75} barrier material, considering [1120] and [0001] directions, in addition to the [1100] direction. Qualitatively, we observed a similar behavior for all orientations, but with a more pronounced electron confinement only for the [1100] and [1120] interface orientations. At least one electron and one hole subband confined in the wells are found, independent of strain and orientation.

In summary, this study provides valuable insights into the intricate interplay between structural and electronic properties

in hexagonal SiGe heterostructures, offering a comprehensive understanding of their behavior under various growth conditions. Actual values for confinement energies and wave function localization have to be taken from relaxed geometries and electronic structures including quasiparticle effects. Models based on finite rectangular potential wells and appropriate carrier masses allow the qualitative discussion of the quantum structures. The simple models that we have developed can be further used to interpret ongoing optical experiments and optimize the performance of new SiGe light-emitting devices.

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