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Electronic properties of germanium quantum films

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The electronic band structures of hydrogen-terminated freestanding nanometer size (0.5–2.4 nm) germanium films have been calculated from first principles for three main low-index orientations. A quantum confinement-induced direct band gap appears for (100) and (111) oriented films, whereas the (110) oriented films are characterized by an indirect band gap. For the same film thickness there is an anisotropy in the fundamental band gap E_g with respect to the film orientation, e.g., $E_g^{\langle 111\rangle}<E_g^{\langle 110\rangle}<E_g^{\langle 100\rangle}$. This is explained in terms of electron effective mass anisotropy. The thickness dependence of the band gap is investigated and the results are fitted to an empirical expression. We find that the band-gap blueshift is determined by the quantum confinement in both valence and conduction bands.

I. INTRODUCTION

Scaling down of semiconductor structures to the nanometer length scales is considered to be a very promising way of getting optoelectronic materials from indirect band-gap semiconductors.[1] The idea is to use quantum confinement in order to transform the gap character from an indirect to a direct one, shift it up, and consequently provide light emission in the visible range. An exciting prospect is that light-emitting devices based on this effect can be compatible with the same technology as the base material. That is why the observation of strong visible luminescence of nanocrystalline silicon has stimulated great research interest in the physics of confined excitons in silicon (for a review see Ref. 2). The main expectation is that the luminescent ultrafine silicon particles may be used in integrated optoelectronic devices, which can be fabricated within the already well-established and highly advanced silicon technology.[3,4] However, the physical origins of nanoparticle luminescence are controversial. A wealth of theoretical papers on the electronic and optical properties of nanostructured silicon has advanced several possible hypotheses. The most popular among them is the quantum confinement effect arising in quantum dots, wires, and films.[5–9] There is also the idea of a dramatic influence of chemical rearrangements at the surface during the sample preparation, i.e., the formation of molecular species containing hydrogen and/or oxygen atoms.[10] Appropriate surface state passivation was also considered to play a key role in the luminescence.[11–13]

Meanwhile, there is also a search for other materials that in a nanocrystalline form can emit light efficiently. Considering compatibility with silicon technology, germanium seems to be a very promising candidate for such investigations. Therefore, there has been great interest in the fabrication and study of Si/Ge superlattices.[14–20] It has been shown that by varying the stress and layer thickness, one may get a direct band gap at the Brillouin zone center in such superlattices.[19,20] Similar phenomena have been predicted for Sn/Ge superlattices[21–24] with a direct band gap, for example, arising in $\mathrm{Sn}_n/\mathrm{Ge}_m$ with $n<m/2$ under tensile strain.[23]

Recently some optical investigations of germanium nanocrystals have been reported.[25–27] On the other hand, theoretical studies of pure germanium nanocrystals have been few. Recently Reboredo and Zunger[28] have reported a study of quantum confinement for surface-passivated germanium quantum clusters using an empirical pseudopotential method. They have shown that below a critical cluster diameter the character of the conduction band minimum (CBM) changes from an L-derived (like in bulk germanium) to an X-derived (like in bulk silicon) state. Hence, there exists a fundamental question whether germanium itself can become intrinsically a direct-gap semiconductor when scaled down to nanodimensions and if quantum confinement can modify the energy gap such that visible light can be emitted.

Historically, studies on quantum confined systems include zero-dimensional (0D) clusters, one-dimensional (1D) wires, and two-dimensional (2D) films. Because of fabrication difficulties 0D and 1D systems often end up highly disordered (see, for example, porous silicon). The situation is less problematic with regard to 2D systems, since molecular beam epitaxy can currently provide ultrathin films with atomic-layer precision. This simplifies the comparison between theoretical and experimental results. From this point of view the band-structure investigations of 2D films seem to be very attractive for a systematic theoretical analysis.

We have theoretically studied the electronic properties of germanium freestanding quantum films with different low-index orientations. The aim of our work was to search for getting a direct band gap in germanium and to determine whether it can reach the visible energy range due to the quantum confinement effect. Band-structure calculations performed for germanium quantum films are presented and discussed below.

II. COMPUTATIONAL DETAILS

Density functional theory electronic structure calculations have been carried out using the linearized augmented plane

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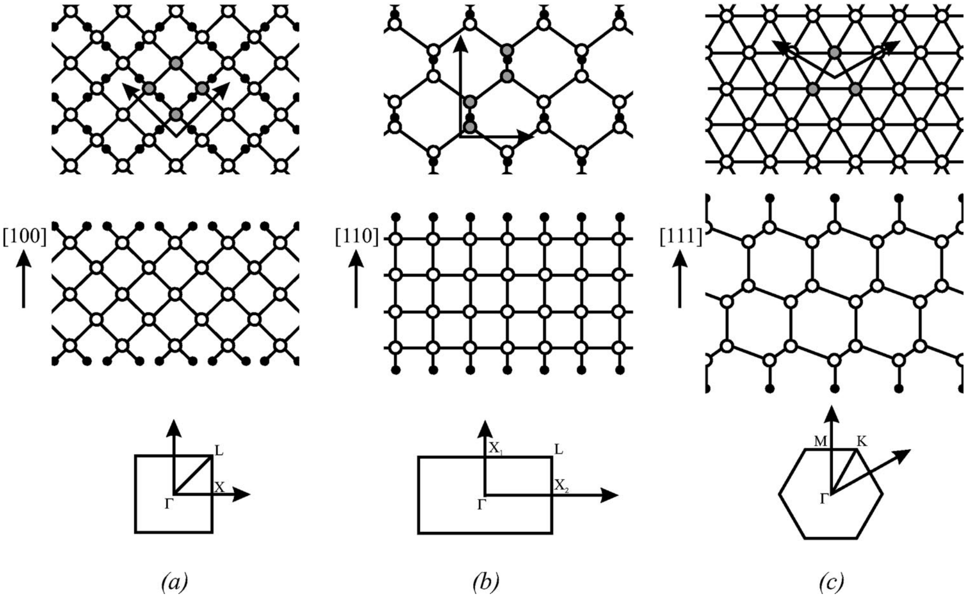

FIG. 1. Cross-section, plane view and Brillouin zone of germanium quantum films with different low-index orientations: (a) (100), (b) (110), and (c) (111). Open circles and dots are germanium and hydrogen atoms, respectively. Gray-colored circles indicate germanium atoms belonging to the unit cell.

wave (LAPW) method with the WIEN97 code.[29] Exchange and correlation potentials were included using the local density approximation (LDA) of Perdew and Wang.[30] This approximation has been established as a very powerful tool for studying ground-state properties of bulk solids, their surfaces, interfaces, and bulk defects. However, the treatment of the excited levels still remains the major shortcoming of LDA that results in a significant underestimation of band gap energies in semiconductors. In particular, for bulk germanium the gap is calculated to be nearly zero.[31] The self-energy corrections obtained by the use of the GW approximation led to a considerable improvement to the band-gap value, though it still remains direct instead of indirect.[32] The principal effect of such corrections is to shift the conduction band up by a certain constant, so-called ''scissors-operator'' shift. In Ref. 33, to remedy the fact that germanium is a semimetal within LDA the authors used a compressed lattice parameter when calculating optical properties. We have also found that the use of the germanium lattice hydrostatically compressed by 2% allows to reproduce qualitatively the band structure of the bulk germanium known from experiments. However, the conduction band energies should be afterwards corrected by the ''scissors-operator'' shift in order to get the fundamental band gap in agreement with experimental data. The upshifts of 0.76 and 0.52 eV are used for an adequate description of the bands related to experimental and compressed lattices, respectively.

Electronic structure calculations have been performed for freestanding (100), (110), and (111) surface-oriented germanium films. Their cross-section and plane view are shown in Fig. 1. The two-dimensional periodicity parallel to the film surface is preserved. Our basic assumption is that the atoms in the films take the same lattice structure and the same interatomic distance as bulk germanium material. There are two surfaces on both sides of the films studied here. Since our interest is in states around the band gap, saturation of all dangling bonds at the surface is essential; otherwise, as it has been shown for silicon nanostructures, the gap would be completely masked by the dangling bond states. In the same manner, as has been often done for silicon, we have chosen to saturate the dangling bonds with hydrogen as the simplest model for actual surface coverage. The bond length between germanium and hydrogen atoms was taken to be 0.1525 nm as in GeH_4 molecule.[34] The calculations are performed along high-symmetry directions in the two-dimensional Brillouin zone illustrated for each film at the bottom of Fig. 1. We use a supercell formed by the germanium film of variable thickness and a vacuum space large enough to avoid interaction between subsequent germanium films. The thickness of the germanium films studied ranges approximately between 0.5 and 2.4 nm.

The muffin tin radius used is 0.106 and 0.042 nm for germanium and hydrogen atoms, respectively. All the calculations are performed with a value of 3.0 for $RK_{\max}$, the parameter controlling the convergence with the number of plane waves. Depending on the film orientation and thickness a self-consistency is achieved using a grid of 8 to 20 **k** points uniformly distributed in the irreducible part of the Brillouin zone.

III. RESULTS AND DISCUSSION

The main features of the electronic properties of germanium films can be derived from their energy-band structures. For this in Fig. 2 we have compiled the band structures of germanium quantum films for three principal orientations and two different thicknesses. Such a compilation helps to highlight similarities and differences observed. The calculation results obtained for both uncompressed and compressed germanium lattices are shown by solid and open dots, respectively.

The principal result of the compression is the upward shift of the conduction bands around the minimum with respect to their positions calculated using the true lattice constant. The dispersion of the valence band seems to be less affected by such compression. However, the character of the bands without and with lattice compression is identical. Thus, we believe that simulations carried out for germanium quantum films using experimental ground-state lattice constant are

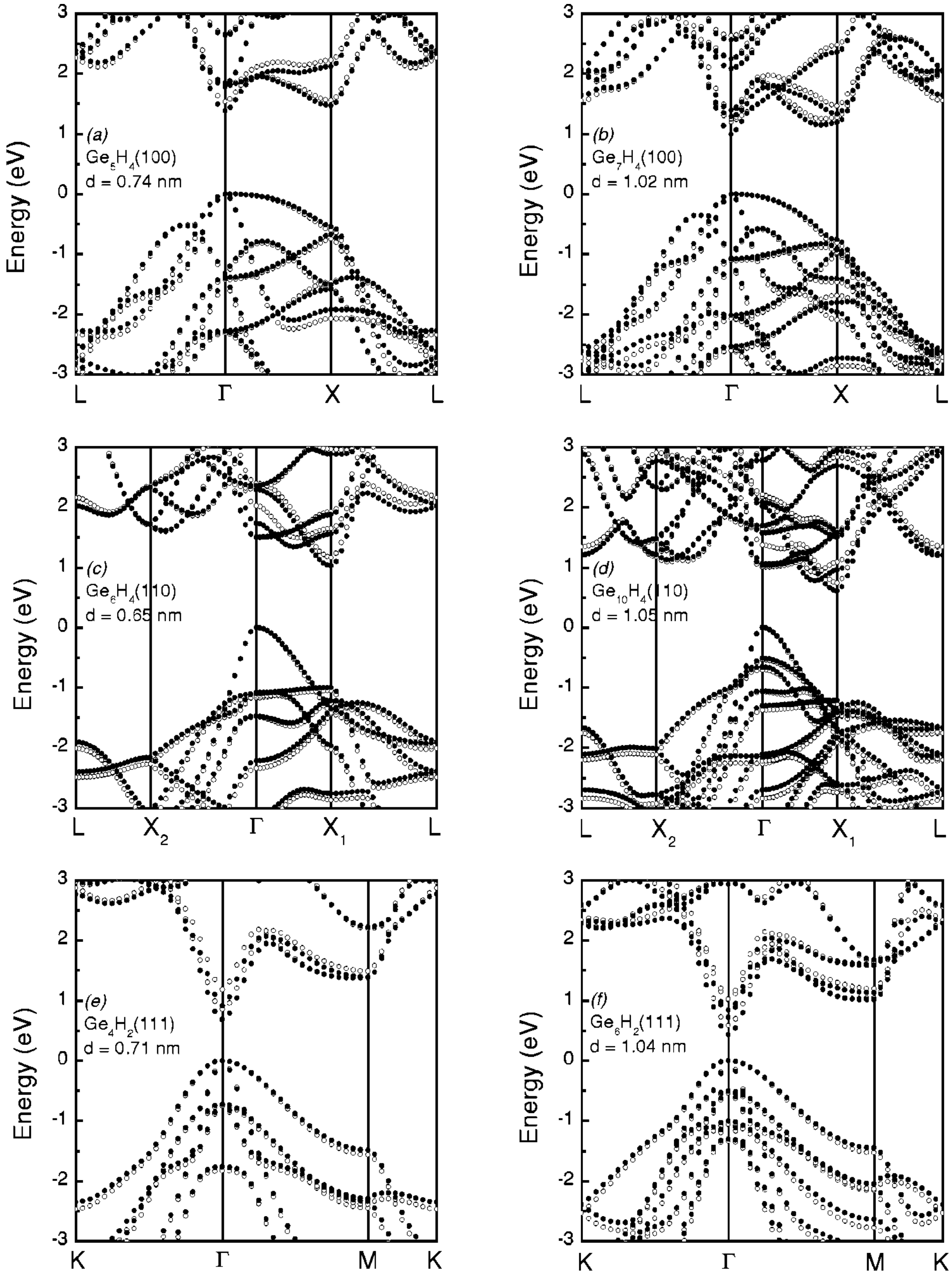

FIG. 2. Electronic band structures of germanium quantum films for different orientations and thicknesses without (solid circles) and with (open circles) lattice compression: (a) Ge_5H_4 (100), (b) Ge_7H_4 (100), (c) Ge_6H_4 (110), (d) Ge_10H_4 (110), (e) Ge_4H_4 (111), and (f) Ge_6H_4 (111).

suitable to obtain reliable results for electronic properties of such nanostructures.

The important feature about the germanium (100) quantum films is that their band structure is characterized by a direct band gap at the Brillouin zone center. However, the indirect CBM is located only few tens of meV higher than the Γ point CBM. One can also assert that the top-most valence band in the vicinity of the Γ point is very flat along the Γ-X axis, thus probably resulting in a remarkable large effective mass for holes in this direction. In the germanium (110) quantum films there are well-resolved global extrema for both valence and conduction bands at the Γ and X_1 points, respectively, thus indicating an indirect gap. The value of the direct gap at the Γ point is almost equal to yet another indirect transition along the Γ-X_2 direction. In the case of the germanium (111) quantum films a pronounced direct transition at the Γ point is observed. There is another local minimum in the conduction band, where the bulk germanium local CBM occurs, along the $\Gamma - M$ direction (that is, the bulk Γ-X direction). The direct gap characteristic appears for all the germanium (100) and (111) quantum films under consideration.

Analysis of the orbital composition shows that states near the valence-band maxima are mainly defined by p states of core germanium atoms. The conduction-band edge, in turn, is found to be dominated by hybridization effects at the germanium surface. Although in the case of (111) and (110) films there is also a large admixture of bulklike germanium atoms to the CBM. It is also worth noting that the dangling bond states do not appear within the band gap region indicating the full passivation of dangling bonds by hydrogen.

In order to represent the main properties of the band structures we concentrate on the results for the fundamental band gap E_g. Figure 3 presents the direct band gap for the germanium (100) and (111) films and indirect band gap for the (110) ones as a function of film thickness. The size-

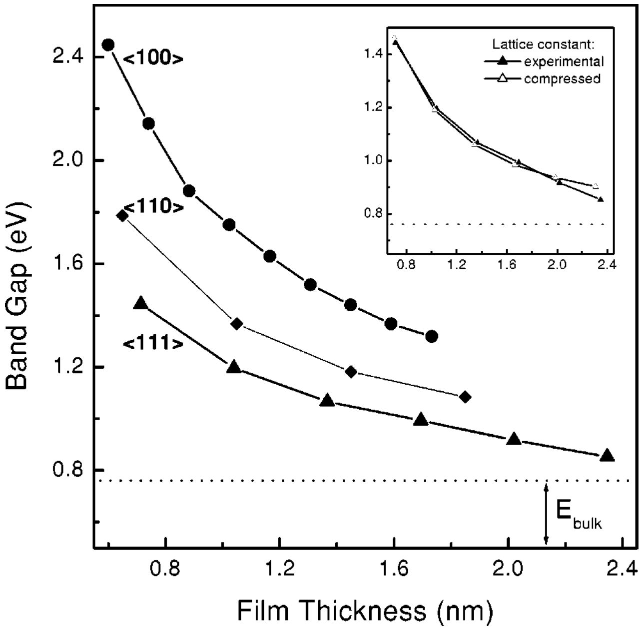

FIG. 3. Thickness dependence of the fundamental band gap in germanium quantum films.

independent self-energy correction as discussed above has been applied. The band gap exhibits rather smooth variation with the structure size. As expected the reduction in the effective film thickness leads to a blue shift in E_g reflecting the quantum size effects. It is also interesting to point out the anisotropy in the fundamental band gap observed for different film orientations: $E_g^{\langle 111\rangle} < E_g^{\langle 110\rangle} < E_g^{\langle 100\rangle}$. In order to understand this effect qualitatively, one may turn to the anisotropy of the conduction band structure in bulk germanium. In terms of electron effective mass m^*, representing the band curvature at the conduction-band minimum, this anisotropy is characterized by the sequence, $m_e^{\langle 111\rangle} = 1.67 m_0 > m_e^{\langle 110\rangle} = 0.38 m_0 > m_e^{\langle 100\rangle} = 0.3 m_0$, where m_0 is the free-electron mass. Since the effective-mass approximation predicts the band gap shift $\Delta E_g \propto 1/m^*$, the quantum confinement in the germanium (100) films should be stronger than in (110) and consequently in (111) films. We think that this is a reason why E_g shows such an anisotropy.

In the inset of Fig. 3 we have plotted the fundamental band gap (including the self-energy correction) of the germanium (111) film versus film thickness calculated both for the true lattice constant and the compressed one. The two curves almost follow each other up to 2.0 nm. The observed discrepancy after 2.0 nm can be attributed to the effects responsible for the band-gap problem in the bulk germanium. However, it confirms our conclusion about the validity of the LAPW method for the calculation of electronic properties of quantum size germanium films.

We have found that the calculated fundamental band gaps for three principal orientations can be fitted within the formula:

$$E_g^{\langle hkl\rangle} = \frac{A_{\langle hkl\rangle}}{d^{n_{\langle hkl\rangle}}} + E_{\text{bulk}}^{\text{Ge}}, \tag{1}$$

TABLE I. Fitting parameters describing the thickness dependence of the fundamental band gap in germanium quantum films [for Eq. (1), where $E_{\text{bulk}}^{\text{Ge}} = 0.76$ eV, d in nm].

Parameter	Orientation $\langle 100\rangle$	 $\langle 110\rangle$	 $\langle 111\rangle$
$A_{\langle hkl\rangle}$	1.00	0.64	0.45
$n_{\langle hkl\rangle}$	1.03	1.10	1.29

where $A_{\langle hkl\rangle}$ and $n_{\langle hkl\rangle}$ are, respectively, a constant term and a power exponent, which depend on the orientation of the film surface; $E_{\text{bulk}}^{\text{Ge}} = 0.76$ eV denotes the energy gap in the bulk germanium. Appropriate values of $A_{\langle hkl\rangle}$ and $n_{\langle hkl\rangle}$ are listed in Table I. Note, that the exponent obtained is different from 2 that would have been expected given a constant effective mass.[35] However, this is not surprising here in view of large confinement energies we find. Rather, our results imply that the parabolic dispersion implicit in the effective mass approximation should be corrected as it exaggerates considerably the increase of the band gap with reduced size. The divergence from the parabolic law in describing the quantum confinement shift of the band gap has been also observed by Zunger and Wang,[9] who made the comparison of effective mass theory versus pseudopotential method for silicon wires and films. The validity of the effective mass theory also becomes questionable if, for example, the wave function of the CBM changes its character with size.[28]

Finally, we have investigated the thickness dependence of the valence and conduction band extrema to ascertain to which extent they contribute to the band-gap blueshift. For this purpose we have compared on a single energy scale the band structures calculated for different film thicknesses taking the 2s core level of the middle germanium atom as a reference energy. For the three orientations considered, Fig. 4 displays the film band structure along the axis where both direct and indirect band gaps occur. For all the cases presented the valence bands shift down while the conduction bands shift up as the thickness of the film is decreased. However, in case of (100) structures this shift is more pronounced for the valence band while the lowest conduction band seems to be less sensitive to the film thickness. This is because the conduction band states are mostly localized at the surface. In case of (110) and (111) oriented films, as discussed above, there is a large contribution to the conduction band edge of the electron states from the bulk-like germanium atoms. This is believed to be a reason that for these films both the valence band and the conduction band seem to be equally responsible for the band gap opening.

IV. CONCLUSION

The LAPW method within the LDA scheme has been applied to study the electronic properties of hydrogen-terminated germanium 2D films. For these structures, the hydrostatic compression of the lattice introduced to compensate for the underestimation of the band gap in the bulk germanium is found not to change qualitatively the results. For this reason, we believe the LAPW approach can be reliably used to calculate the electronic properties of germanium nanostructures with the true lattice constant. It is predicted

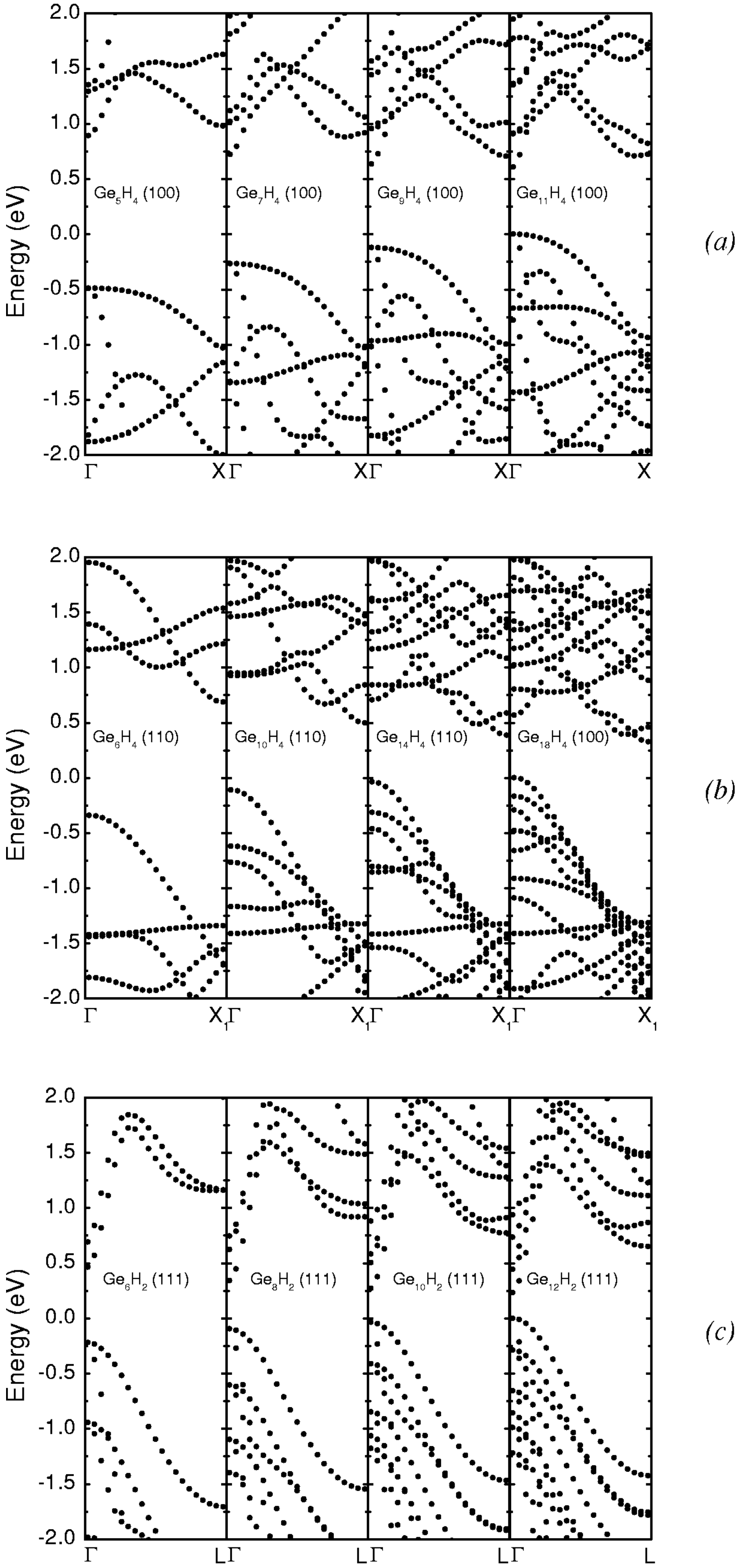

FIG. 4. Evolution of the band structure of germanium quantum films with the decrease of the film thickness: (a) (100), (b) (110), and (c) (111).

that quantum confinement makes the band gap direct in (100) and (111) germanium films while (110) films remain indirect. The anisotropy of the energy gap with respect to the film orientation is qualitatively explained in terms of electron effective mass. The film-thickness dependence of the fundamental band gap is investigated for all the three film orientations. An empirical expression for the energy gap in terms of the film thickness is then extracted. We find that the confinement-induced increase in the band gap in (100) films is largely due to the shift of the valence-band edge. Conversely, in (110) and (111) films the shifts of the valence and the conduction bands are compatible. From the results presented one may conclude that the folding of the energy bands onto the germanium film surface due to the quantum confinement effect can make the band gap direct. However, a direct band-gap structure is not adequate to ensure that a particular nanostructure will have a strong optical transition. Therefore, calculations of optical properties are needed to extend the knowledge about germanium quantum films. We hope that our results will stimulate further theoretical work on these structures.

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