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Stability and electronic structure of ultrathin-layer superlattices: $(\mathrm{GaAs})_n/(\mathrm{AlAs})_n$

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A first-principles total-energy calculation has been performed for ultrathin-layer (001) superlattices, $(\mathrm{GaAs})_n/(\mathrm{AlAs})_n$ (n layers of GaAs alternating with n layers of AlAs, with $n=1$ and 2). The total energies for the superlattices are higher than the averaged total energies of GaAs and AlAs by about 5 meV per atom. This small difference in energy results from the efficient screening of the valence electrons at the As interface layers. The calculated total energy of the alloy semiconductor $\mathrm{Ga}_{0.5}\mathrm{Al}_{0.5}\mathrm{As}$, in turn, is higher than that of the superlattices by 88 meV per atom. An indirect gap in $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$ and a direct gap in $(\mathrm{GaAs})_2/(\mathrm{AlAs})_2$ are inferred from the calculated energy bands.

Recent developments in microfabrication are opening up a new stage in science where artificial materials having desired properties are constructed for particular studies and applications. Progress[1] in the techniques of molecular-beam epitaxy, metal-organic chemical-vapor deposition, or atomic-layer epitaxy enables us to use layer-by-layer epitaxial growth in constructing new artificial materials. It is possible that new electronic devices with favorable characteristics can be designed[2] with the aid of this layer-by-layer controllability. Furthermore, even atom-by-atom manipulation is now being discussed[3] in a realistic manner, and a new realm of condensed-matter physics could emerge[4] from these developments in technology.

Among such new materials, the semiconductor (001) superlattice $(\mathrm{GaAs})_m/(\mathrm{AlAs})_n$ consisting of m layers of GaAs alternating with n layers of AlAs has been intensively investigated because of its potentially important applications. The period of the superlattice in the growth direction can be very short, and now it is argued that even the one-by-one superlattice, $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$, has been realized at some laboratories.[5–7] Nevertheless, the experimental data on such ultrathin-layer superlattices are not necessarily identical to each other: The peak energy of the photoluminescence of $(\mathrm{GaAs})_m/(\mathrm{AlAs})_n$ diverges by several tens of meV for the same value of (m,n).[5,8] Further, it is as yet unclear whether $(\mathrm{GaAs})_m/(\mathrm{AlAs})_n$ is a direct-gap or an indirect-gap semiconductor,[5–9] although the calculations[10–12] performed so far within the local-density-functional formalism give comparatively converged results. A first-principles calculation which can provide reliable information thus plays an important role in clarifying the physical properties of the new artificial materials. Moreover, it is of interest whether the ultrathin-layer superlattices are stable, in particular against alloying of the constituent Ga and Al atoms. Kuan *et al.*[13] have observed an ordered $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$ structure even in spontaneous growth, whereas the recent local-density calculations[12,14] for $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$ suggest intrinsic instability of this superlattice structure.

In the present paper, we have performed an accurate first-principles total-energy calculation[15,16] for $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$ and $(\mathrm{GaAs})_2/(\mathrm{AlAs})_2$ along with GaAs, and AlAs, and the alloy semiconductor $\mathrm{Ga}_{0.5}\mathrm{Al}_{0.5}\mathrm{As}$, with the use of norm-conserving pseudopotentials and a well-converged plane-wave basis set. The lattice constant for each structure is determined by minimizing the total energy within the restriction of a cubic zinc-blende structure. The obtained total energy for both $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$ and $(\mathrm{GaAs})_2/(\mathrm{AlAs})_2$ is slightly higher than the averaged total energies of GaAs and AlAs. However, the differences in total energy per atom are comparable to or less than $k_B T$. This remarkably small difference in energy can be traced to the charge redistribution in the superlattice structure. The alloy semiconductor $\mathrm{Ga}_{0.5}\mathrm{Al}_{0.5}\mathrm{As}$ is treated in the virtual-crystal approximation with the present local-density-functional framework. The calculated total energy of $\mathrm{Ga}_{0.5}\mathrm{Al}_{0.5}\mathrm{As}$ is higher than that of the superlattices by 88 meV per atom. The energy-band structure of the superlattice is also discussed in the present paper.

Let us first give a brief description of the present calculation.[16] Norm-conserving relativistic pseudopotentials[17] are constructed by fitting the results for valence states from an all-electron atomic calculation. The charge density of the valence electrons is determined within the local-density-functional formalism.[18] The Ceperly-Alder form[19,20] is employed for the exchange-correlation energy in the local-density approximation. Self-consistency is achieved within 10^{-2} meV for the mean difference between the input and the output crystal potentials. The wave functions are expanded in terms of a plane-wave basis set. The number of plane waves is determined by the fixed kinetic energy cutoff of 12.6 Ry (corresponding to about 450 plane waves for the one-by-one superlattice structure). This kinetic energy cutoff is enough to assess the total-energy difference among several structures, although a cutoff energy of more than 20 Ry is necessary to obtain the absolute value of the total energy (i.e., cohesive energy).[16] The superlattice structure is a tetragonal lattice with two lattice parameters a and c, and further the bond lengths of Ga—As and Al—As can be different. We assume here, however, that the structure is cubic zinc-blende [i.e., $c=\sqrt{2}a$ for $(GaAs)_1/(AlAs)_1$ and $c=2\sqrt{2}a$ for $(GaAs)_2/(AlAs)_2$], and that the two types of bond length are identical. Thus, one lattice constant $a_0=\sqrt{2}a$ is left to be optimized. To assure the relative energy difference between the superlattice structures and the constituent bulk compound, the calculation for GaAs, AlAs, and $Ga_{0.5}Al_{0.5}As$ is performed in the tetragonal unit cell of the one-by-one superlattice structure.

In Table I, the calculated total energy is shown for $(GaAs)_1/(AlAs)_1$, $(GaAs)_2/(AlAs)_2$, GaAs, and AlAs. When the lattice constant a_0 is fixed to the value of 5.662 Å (the averaged value of the calculated lattice constants of GaAs and AlAs with fcc unit cells), the total energies of $(GaAs)_1/(AlAs)_1$ and $(GaAs)_2/(AlAs)_2$ are higher than the averaged total energies of GaAs and AlAs by several meV/atom. Then, the lattice constant of $(GaAs)_1/(AlAs)_1$ is optimized by minimizing the total energy. The resulting lattice constant is 5.673 Å, which is very close to the averaged lattice constants of GaAs and AlAs. Thus, the resulting total energy for $(GaAs)_1/(AlAs)_1$ with the optimized lattice constant is almost identical to that with the averaged lattice constant. The optimized lattice constants of GaAs and AlAs with the tetragonal unit cell are 5.609 and 5.725 Å, respectively, and the total energies of GaAs and AlAs are lowered by about meV/atom by this optimization of the lattice constant. Then the final total energy of $(GaAs)_1/(AlAs)_1$ is higher than the averaged value of the total energies of the constituent bulk semiconductors by 5.3 meV/atom.

In any case, the difference in total energy between the superlattices and the constituent bulk semiconductors is very small, and is comparable to or less than $k_B T$. This results from the remarkably efficient screening of the valence electrons (Fig. 1). In the superlattice structure, electrons are transferred from the AlAs layers to the GaAs layers because of their difference in electron negativity.[21] The calculated charge excess in the GaAs layer is 0.051 electrons for $(GaAs)_1/(AlAs)_1$ and 0.057 electrons for $(GaAs)_2/(AlAs)_2$. This closeness in the values indicates that the charge transfer occurs primarily at the interface. This can be clearly demonstrated in Fig. 1. An appreciable redistribution of charge density can be seen only at the As atoms at the interface layers. In other words, the charge density in the majority of the system remains unchanged compared with bulk GaAs and AlAs, and we thus obtain approximately the same total energy for the superlattice structures and the bulk semiconductors. This efficient screening of valence electrons in turn supports the validity of the appropriate effective-mass calculation for sufficiently thick superlattices.

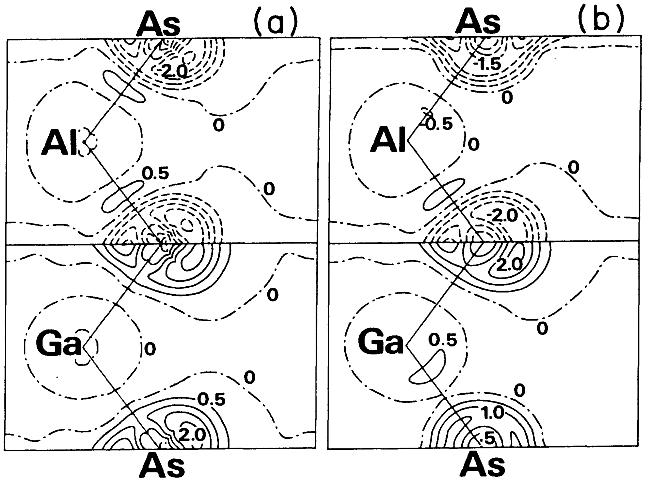

FIG. 1. Valence-electron charge density (in electrons per unit cell of a one-by-one superlattice structure) for (a) $(GaAs)_1/(AlAs)_1$ and (b) $(GaAs)_2/(AlAs)_2$ displayed in a $(\bar{1}01)$plane. The density is subtracted from that of AlAs (the upper part) and that of GaAs (the lower part).

The alloy semiconductor $Ga_{0.5}Al_{0.5}As$ is also studied in the virtual-crystal approximation within the present local-density-functional formalism: The averaged pseudopotential of Ga and Al is considered to be the pseudo-

TABLE I. Calculated total energy per unit cell of the one-by-one superlattice structure. The total energies (in Ry) with $a_0=5.662$ Å and with the optimized lattice constant (the fourth column) are shown in the second and third columns, respectively.

	Total energy (Ry)		
	$a_0=5.662$ Å	$a_0=a_{0,\mathrm{opt}}$	$a_{0,\mathrm{opt}}$ (Å)
GaAs	−34.3962	−34.3972	5.609
AlAs	−33.7805	−33.7813	5.725
$(GaAs)_1/(AlAs)_1$	−34.0877	−34.0877	5.673
$(GaAs)_2/(AlAs)_2$	−34.0876		
$Ga_{0.5}Al_{0.5}As$	−34.0616	−34.0617	5.678

TABLE II. Calculated energy of the conduction-band minimum relative to the top of the valence bands (in eV).

	Γ	L	X
GaAs	0.79	1.22	1.52
AlAs	2.47	2.48	1.50
$(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$	1.27	1.26 (R_1)	1.47 (M)
$(\mathrm{GaAs})_2/(\mathrm{AlAs})_2$	1.34	1.64 (X)	1.45 (M)
$\mathrm{Ga}_{0.5}\mathrm{Al}_{0.5}\mathrm{As}$	1.48	1.69	1.46

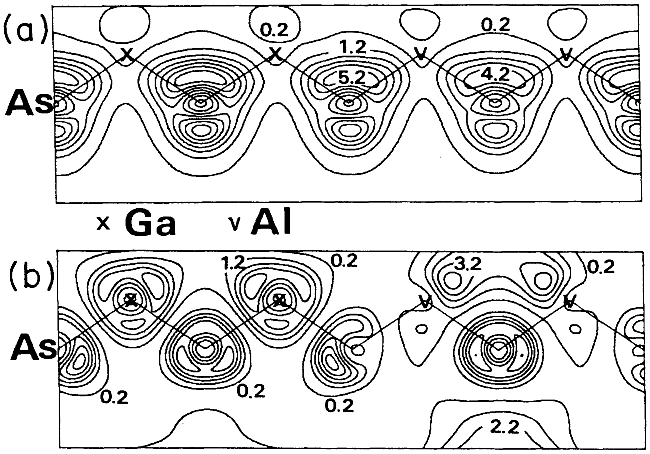

FIG. 2. Contour on the $(\bar{1}01)$ plane of the square of the wave functions at the Γ point of (a) the highest valence and (b) the lowest conduction bands of $(\mathrm{GaAs})_2/(\mathrm{AlAs})_2$ (in electrons per unit cell).

potential of the virtual cation atom, and valence electrons are distributed self-consistently within the local-density approximation. The optimized lattice constant is 5.678 Å, and the resulting total energy is −34.0617 Ry per unit cell of the one-by-one superlattice (Table I). Thus the total energy of $\mathrm{Ga}_{0.5}\mathrm{Al}_{0.5}\mathrm{As}$ is higher than that of the superlattices by 88 mRy/atom. This suggests that the superlattice structure is stable at low temperature against alloying of the constituent Ga and Al atoms, although the barrier for atomic diffusion through the interface may be a relevant quantity in discussing the stability.

We now turn to the energy band structure of the superlattices. It is known[22–24] that the local-density approximation underestimates the energy gap considerably. However, the overall structure of the energy bands is well described in this approximation.[16] Thus, the relative locations of the eigenstates in the conduction bands of the superlattices and the constituent bulk semiconductors are considered to be described in the present calculation. In Table II, the calculated energies[25] of the conduction bands relative to the tops of the valence bands are shown for $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$ and $(\mathrm{GaAs})_2/(\mathrm{AlAs})_2$, along with those of GaAs, AlAs, and $\mathrm{Ga}_{0.5}\mathrm{Al}_{0.5}\mathrm{As}$. For $(\mathrm{GaAs})_2/(\mathrm{AlAs})_2$, the minimum of the conduction bands lies at the Γ point, whereas the minimum lies at the L point for $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$. This feature is essentially the same in the previous local-density calculation.[10–12] In the local approximation the energy gap at the Γ point is underestimated compared with the gap at the L or X point in the cases of GaAs and AlAs.[16] Thus, we are inclined to argue that $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$ is an indirect-gap semiconductor with conduction-band energy a minimum at the L point. In Fig. 2, the wave functions of the lowest conduction band and the highest valence band at the Γ point are shown for $(\mathrm{GaAs})_2/(\mathrm{AlAs})_2$. The wave function of the valence band consists primarily of the p_x and p_y states of the As atoms, whereas that of the conduction band is located at both the Ga and As sites. Comparison of the wave functions of the conduction bands for the superlattice structure with those for the constituent compound semiconductors leads to the conclusion that the conduction-band wave function for $(\mathrm{GaAs})_2/(\mathrm{AlAs})_2$ has mainly Γ character in the GaAs layer, while it has both Γ and X characters in the AlAs layer. This feature could cause weak photoluminescence intensity even for the direct-gap $(\mathrm{GaAs})_2/(\mathrm{AlAs})_2$.

In conclusion, the total energies of the superlattices, $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$ and $(\mathrm{GaAs})_2/(\mathrm{AlAs})_2$, are higher than the averaged total energies of GaAs and AlAs. However, the difference in energy is comparable with or less than the temperature. The total energy of the alloy semiconductor $\mathrm{Ga}_{0.5}\mathrm{Al}_{0.5}\mathrm{As}$ in turn is higher than that of the superlattice structure. This suggest that the superlattice, once constructed, is stable at low temperature against diffusion of the constituent Ga and Al atoms. Finally, the obtained band structure indicates that $(\mathrm{GaAs})_2/(\mathrm{AlAs})_2$ is a direct-gap semiconductor, whereas $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$ is an indirect-gap semiconductor.

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