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Giant birefringence in zinc-blende-based artificial semiconductors

J.-M. Jancu,[1,2] A. Vasanelli,[1] R. Magri,[1,3] and P. Voisin[1]
[1]*Laboratoire de Photonique et de Nanostructure, CNRS, route de Nozay, F91000, Marcoussis, France*
[2]*Scuola Normale Superiore and INFM, Piazza dei Cavalieri 7, I-56126 Pisa, Italy*
[3]*S-INFM and Dipartimento di Fisica, Università di Modena e Reggio Emilia, via Campi, Modena, Italy*

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We use extended-basis empirical tight-binding calculations and examine the anisotropy of the refractive index in ultrashort-period superlattices of materials sharing no common atom. We find that a strong birefringence can be engineered in these articial semiconductors, allowing phase matching for frequency difference generation. The prominent role of epitaxial constraint and bond-length alternation is evidenced.

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III–V and II–VI semiconductors have a remarkable potential for applications in nonlinear optics, because they offer a unique combination of high second-order optical nonlinearities (>100 pm/V), good thermal properties, and high flexibility in the design of epitaxial heterostructures such as electrically tunable optical waveguides. Unfortunately, this potential cannot be used in practice because the isotropic nature of cubic semiconductors inhibits birefringence: due to the dispersion of the refractive index, optical waves of different wavelengths are unable to remain phase matched over long distances as required for efficient frequency mixing based on the optical nonlinearities in the transparency region.[1]

Presently, there is a strong motivation to solve this long-standing phase matching problem for it is an intellectual challenge opened more than 40 years ago, and also because compact, field-tunable semiconductor-based optical parametric oscillators would have a variety of applications. The most successful attempts to date[2] have been based on the “shape birefringence” of layered structures that results from the different boundary conditions for the electromagnetic fields across a dielectric interface. By using material pairings with a large refractive index difference, like GaAs and aluminium oxide, one can engineer optical waveguides with impressive birefringence. Other lines of active research are the design of quasiphase matching by periodic sign reversal of the nonlinear susceptibility and the achievement of modal phase matching by Bloch mode engineering.[3,4] Here, we discuss a conceptual approach based on the direct implementation of strong birefringence in artificial semiconductors. To this end, we consider short-period [001]-oriented superlattices made of binary constituents that share no common atom (NCA-SLs).

NCA quantum well (QW) structures such as InAs-AlSb,[5] (InGa)As-InP[6,7], and BeTe-ZnSe[8] have recently attracted attention because they display an in-plane optical anisotropy illustrating the breakdown of the rotational symmetry at semiconductor (001) interfaces, a fundamental property whose possible impact on optical properties had been overlooked for many years. A NCA interface between materials C1A1 and C2A2 displays two remarkable features: first, the reduced C_{2v} point-group symmetry, common to all interfaces, which is due to the alternation of “forward” and “backward” bonds lying in the (110) (or X') and (-110) (or Y') planes, respectively; second, an abrupt NCA interface introduces a bonding type, either Al-C2 or A2-C1, otherwise absent from the material constituents. In general these interfacial bonds undergo considerable $(3\%-5\%)$ strain. Until now, the attention has mainly focused on explanation of the zone-center mixing of heavy- and light-hole states[6,8–10] and the related in-plane polarization anisotropy of interband transitions. In fact, the weak birefringence observed in the transparency region of 10 nm wide QWs was found in good agreement with the Kramers-Kronig transform of the dichroism measured in the near-gap region.[11] This demonstrates that in this case, the higher transitions near the E1 and E2 gaps (which are responsible for the large values of the optical index) do not contribute significantly to the optical anisotropy. Conversely, in the limit of ultrashort-period superlattices (USPSLs), resulting from alternation of C1A1 and C2A2 monolayers, one should obtain a strongly anisotropic artificial crystal with potentially large optical differences between the [110] (x'), [-110] (y'), and [001] (z) axes. Obviously, quantitative evaluation of the optical properties in USPSLs is beyond the possibilities of the $\mathbf{k}\cdot\mathbf{p}$ theory. Instead, reliable atomistic approaches are required, allowing for a precise modeling of the entire Brillouin zone even in the presence of strongly strained chemical bonds. Suitable approaches include, e.g., *ab initio* or empirical pseudopotential methods, or elaborate tight-binding (TB) techniques. Albeit empirical methods show a much better computational efficiency, they are of course sensitive to parametrization issues. In order to propose reliable calculations, we have chosen here to focus on combinations of bulk materials where band parameters can be used for unambiguous empirical parametrizations. More specifically, we discuss results of InAs/AlSb [001]-oriented SLs, for they present a good compromise between knowledge of parameters, technical feasibility, and suitability for waveguide applications. Electronic band structure calculations were performed within the tight-binding approximation using an $sp^3d^5s^*$ nearest neighbor model that includes spin-orbit coupling.[12] This 40-band tight-binding model adequately reproduces chemical trends, dielectric functions, and photoelastic coefficients of III–V semiconductors,[13] which is a prerequisite for the present study. Optical response is calculated within the independent

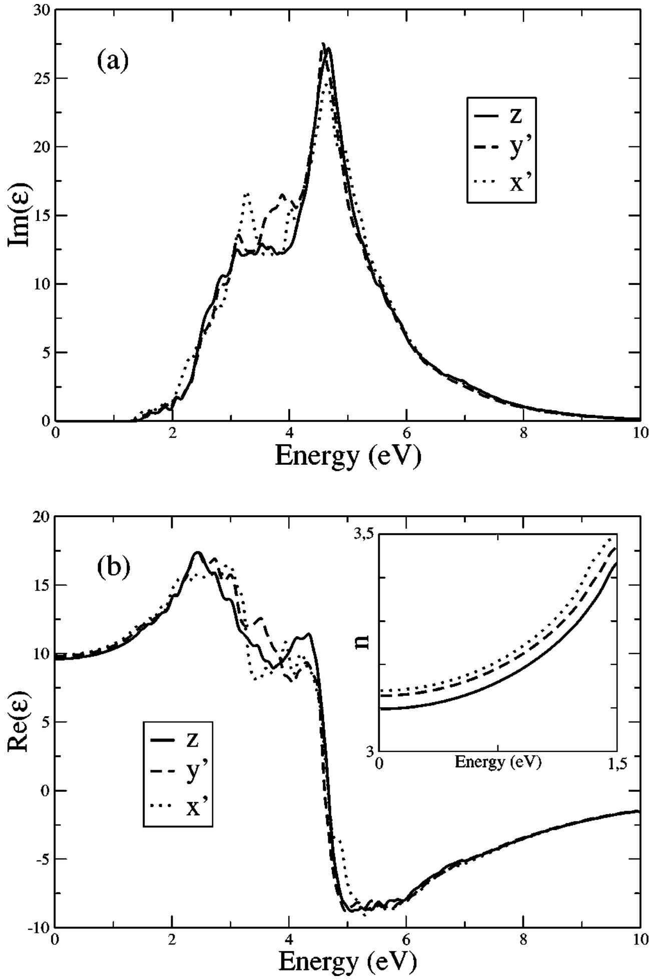

FIG. 1. Imaginary (a) and real (b) parts of the dielectric function for a C_{2v}-asymmetric $(\mathrm{InAs})_2/(\mathrm{AlSb})_2$ superlattice for light polarized perpendicular (x' and y') and parallel (z) to the [001] direction. The SL is lattice matched on GaSb(001) and thickness is defined in monolayers. Inset shows the low energy region of the index dispersion.

TABLE I. Static birefrigence of ultrashort-period superlattices lattice matched on GaSb(001) (a,b,c,e,f) and on a GaAs substrate (d): asymmetric SL (a); symmetric SL with a common-As interface (b,f); symmetric SL with a common-Sb interface (c).

Structure	Symmetry	Substrate	$\delta n_{z-x'}$
$(\mathrm{InAs})_2/(\mathrm{AlSb})_2$ [a]	C_{2v}	GaSb	−0.031
$(\mathrm{InAs})_2/(\mathrm{AlSb})_2$ [b]	D_{2d}	GaSb	−0.106
$(\mathrm{InAs})_2/(\mathrm{AlSb})_2$ [c]	D_{2d}	GaSb	+0.028
$(\mathrm{GaAs})_2/(\mathrm{AlAs})_2$ [d]	D_{2d}	GaAs	−0.0086
$(\mathrm{GaAs})_2/(\mathrm{AlAs})_2$ [e]	D_{2d}	GaSb	−0.263
$(\mathrm{InAs})_1/(\mathrm{AlSb})_1$ [f]	D_{2d}	GaSb	−0.182
$(\mathrm{InAs})_3/(\mathrm{AlSb})_3$ [f]	D_{2d}	GaSb	−0.061
$(\mathrm{InAs})_4/(\mathrm{AlSb})_4$ [f]	D_{2d}	GaSb	−0.040

particle approximation using a Pierls-coupling TB scheme[14] that guarantees gauge invariance and charge conservation. We use a dense mesh of 8200 k points uniformly distributed over the irreductible wedge of the superlattice Brillouin zone and individual transitions are dressed with a gaussian broadening of 0.1 eV in order to get smooth optical spectra. The SL Hamiltonian includes strain effects and requires the unstrained valence band offsets as the only external parameters. We use values from first-principles calculations[15] that give good agreement with the available experimental data.

Figures 1(a) and 1(b) shows the calculated dielectric functions (respectively, imaginary and real part) of the $(\mathrm{InAs})_2/(\mathrm{AlSb})_2$ superlattice, for light polarized along the x', y', and z axes. The growth sequence is In—As═In—As═Al—Sb═Al—Sb═, where "—" and "═" indicate chemical bonds in the X' and Y' planes, respectively. The in-plane lattice parameter is that of a GaSb substrate and the positions of atomic planes are determined from classical elasticity. They differ only slightly from the positions given by the valence force field model and we checked that the latter yield unsignificant changes in the dielectric functions. The In—Sb(Al—As) interfacial bonds are highly compressed (stretched), while the InAs and AlSb bulk-like bonds are essentially unstrained. Spectra of Figs. 1(a) and 1(b) evidence complex differences between polarizations. However, the predicted trends of the dielectric tensor elements in the transparency region are clearly observed in the inset of Fig. 1(b) that shows a blowup of the low-energy part of the refractive index spectrum. The optical anisotropy is mainly reflected by the large difference between z and x' polarizations: $\delta n_{z-x'}=n_z-n_{x'}=-0.031$ (see Table I). A smaller but sizeable birefringence is also observed between the two x' and y' in-plane directions: $\delta n_{y'-x'}=n_{y'}-n_{x'}=+0.012$. The latter is a direct illustration of the reduced C_{2v} symmetry related to different interface bonding contributions. These results suggest that the dominant ingredient of birefringence is associated with the D_{2d} rather than the C_{2v} character of the growth sequence. To study this point further, we have examined the SL with the growth sequence: In—As═In—As═Al—Sb═Al—As═, where the common-As interfaces are obtained by an antimony-for-arsenic substitution at the end of the supercell.

Experimentally, such an atomic scale control over the growth sequence is possible through the choice of low temperature conditions[16] and shutter manipulations during molecular beam epitaxy.[17] We term this structure "2/2, 2As" and by extension "n-n, 2As" for $(\mathrm{InAs})_n/(\mathrm{AlSb})_n$ superlattices. Such a structure has D_{2d} symmetry, characterized by the same number of each type of bond in the X' and Y' planes. The refractive index displayed in Fig. 2(a) shows no difference between the x' and y' polarizations, as required by D_{2d} symmetry, but an enhanced optical anisotropy between the z and in-plane polarizations: $\delta n_{z-x'}=-0.1$ (Table I). Similarly, the "2/2, 2Sb" structure defined by common-Sb interfaces, shows a birefringence $\delta n_{z-x'}=+0.028$ [Fig. 2(b)]. Note that the averaged birefringence $\delta n_{z-x'}$ of 2/2, 2As and 2/2, 2Sb is nearly equal to that of the C_{2v}-asymmetric 2/2 superlattice (Table I). It is worth mentioning here a remarkable property of the ultrathin interfacial InSb layers: they form deep potential wells which would trap the fundamental valence state of the superlattice. The occurrence of native interface states in such NCA SLs is a rather interesting feature

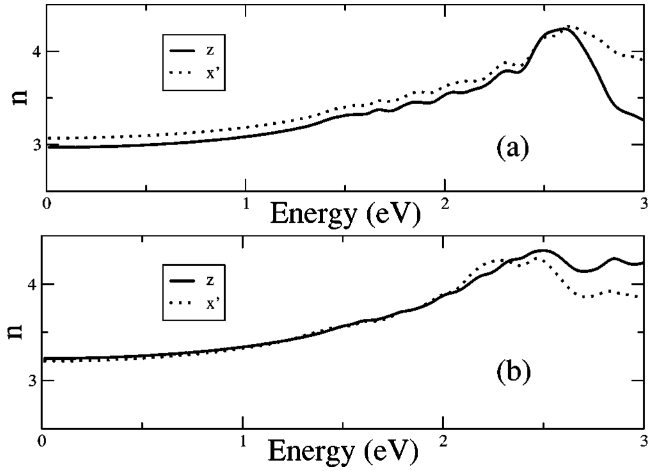

FIG. 2. Panel *a*: optical index dispersion for the D_{2d}-symmetric $(InAs)_2/(AlSb)_2$ 2/2, 2As superlattice grown on GaSb(001) with common-As interfaces. Panel b: same for the 2/2, 2Sb structure. In-plane birefringence $n_{x'}$-$n_{y'}$ is not allowed by D_{2d} symmetry.

that would deserve experimental investigations. Nevertheless, it does not govern the birefringence effect investigated here. Common-anion [001]-oriented superlattices, like GaAs/AlAs, also have D_{2d} symmetry inherent to the tetragonal geometry. However, we calculate a negligible birefringence $\delta n_{z-x'}=-0.009$ for a $(GaAs)_2/(AlAs)_2$ superlattice on a GaAs substrate, in agreement with experimental[18] and *ab initio*[19] results. The reason appears to be the absence of local strain that preserves the tetrahedral order in the local environment. Thus, strain associated with specific interfacial bonds in the NCA heterostructures would be the leading factor in the calculated birefringence. In order to prove this point directly, we simulated two supercell configurations. First, we calculated the optical anisotropy of the $(InAs)_2/(AlSb)_2$ structure, where the atomic positions of chemical species are those of fictitious *c*-GaSb lattice. In this (nonequilibrium) configuration, a much smaller birefringence is found: $\delta n_{z-x'}=-0.013$ and $\delta n_{y'-x'}=-0.007$. This is in agreement with *ab initio* results[7] which showed that neglecting the strain at the interface bonds leads to an underestimation of the superlattice optical anisotropy. Second, modeling bulk GaAs by a fictitious supercell where the relaxed positions of 2/2, 2As were used, we obtained a large optical anisotropy: $\delta n_{z-x'}=-0.055$. These results show that the atomic chemical environment plays a secondary role whereas the local strain around the atoms is of utmost importance. Yet, it should be stressed that the birefringence calculated for realistic strained interfacial bonds is much larger than an average over the piezobirefringence of the bulk consituents. Apparently, the small piezobirefringence of cubic semiconductors stems from a nearly complete cancellation of opposite contributions arising from different regions of the Brillouin zone.[20] The situation changes when starting from a reduced symmetry like D_{2d}. We assessed such effects by contrasting the optical anisotropy of the "1/1, 2As" superlattice (i.e., ordered $Al_{0.5}In_{0.5}As$ alloy) grown on a GaSb substrate, $\delta n_{z-x'}=-0.18$, with that of cubic-$Al_{0.5}In_{0.5}As$ (defined by the virtual crystal approximation) under the same epitaxial condition, $\delta n_{z-x'}=-0.08$. Along the same line, it is also useful to study the piezobirefringence of the USPSL itself. We consider again the 2/2, 2As structure. Due to the two planes of short Al-As bonds in a surrounding of much longer In-As and Al-Sb bonds, the entire SL is strained as a whole (1.8%) in order to match the lattice constant of a GaSb substrate. With a free standing configuration (i.e., relaxed in-plane lattice constant), the birefringence lowers to $\delta n_{z-x'}=-0.015$, which results from opposite strain fields in the quantum structure. On the contrary, a tensily strained $(GaAs)_2/(AlAs)_2$ superlattice grown on a GaSb substrate displays a strong birefringence $\delta n_{z-x'}=-0.25$.[21] Finally, we investigated the birefringence of the "n/n, 2As" SLs and found that it decreases like $1/n$, that is just like the average strain in the SL. The calculated static birefringences are summarized in Table I. From the whole set of numerical results, we conclude that USPSLs have a weak intrinsic anisotropy but their piezobirefringence is greatly enhanced compared to bulk materials. Thus, the sign as well as the magnitude of the birefringence are tailorable. The effect of the bond chemistry (NCA versus common anion systems) seems to play a secondary role, except for the intrinsic strain that it introduces. Finally, we found that, at least up to $n=5$, the piezobirefringence properties do not depend appreciably on the superperiod. Thus, strained common anion SLs with reasonably large periods can display the desired strong birefringence. Note that the local field effects (ultimately responsible for the shape birefringence of layered structures) which have been neglected in the present calculations, would play a significant role for large-period superlattices.[19] Electron-hole interactions, also neglected here, are important for understanding the spectral functions near resonances.[22,23] However, they give a rather small correction to the static dielectric constant of cubic semiconductors (e.g., 4% for GaAs) and consequently should not significantly affect the birefringence properties we are concerned with here.

Coming back to the problematic of phase matching for frequency difference generation, it is clear that the results shown in Fig. 2 allow phase matching of a z-polarized (transverse magnetic) wave in the near gap region (~1.2 eV) with x-polarized (transverse electric) waves in the midgap range: $n_z(1.2\text{ eV})=n_{x'}(0.6\text{ eV})$. The large dispersion of the refractive index around the gap would allow the tuning of the phase matching condition in a wide range of wavelengths, and the field dependence of the optical index near resonance would provide an additional degree of freedom for fine tuning.

In summary, we have shown that strained ultrashort period superlattices can be used to engineer a large birefringence of ~0.1 offering a conceptual solution to the long standing problem of phase matching for frequency mixing in cubic semiconductors. Many different systems based on III–V or II–VI materials have to be evaluated in order to select the material combination best suited to a specific application. Semiempirical atomistic calculations, and in particular the advanced tight-binding technique used here, are a very efficient tool for this purpose. In some cases, direct quantitative comparison with *ab initio* calculations should be possible and would provide an independent test of the predictions presented here. Such superlattice structures with an ultrashort period are close to the present limits of epitaxy, and their successful growth will certainly be a considerable challenge. Citing Esaki and Tsu,[24] "it may be a formidable task to construct the proposed superlattice, but efforts directed to this end will open new areas of investigation in the field of semiconductor physics".

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