Full-band-structure calculation of $\vec{\vec{\epsilon}}_2(\omega)$ and $\vec{\vec{\chi}}^{(2)}(-2\omega;\omega,\omega)$ for $(GaAs)_n/(GaP)_n$ ($n=1,2$) superlattices on GaAs(001) substrates

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We have carried out a full-band-structure calculation of the frequency-dependent dielectric tensor and second-harmonic-generation coefficient in $(GaAs)_n/(GaP)_n$ ($n=1,2$) superlattices on GaAs(001) substrates. We use a linear combination of Gaussian orbitals technique, in conjunction with the $X\alpha$ method for constructing the potentials of the constituent *bulk* materials, to calculate the electronic band structures and momentum matrix elements of these superlattices. The optical properties are then evaluated by utilizing a linearized tetrahedra sampling method. Our results indicate that the anisotropy in these materials is mostly due to tensile strain in the GaP layers. More importantly, in contrast to the $(GaAs)_n/(AlAs)_n$ short-period superlattices, the effect of the strain here is to considerably enhance the second-harmonic response as compared with the average of the responses of the constituent bulk materials.

In the past few years the electronic properties of the strained $(GaAs)_m/(GaP)_n$ superlattices (SLS) have been the focus of a number of experimental[1-3] and theoretical studies.[4,5] Part of the interest stems from the fact that the electronic and optical properties of these SLS can be greatly modified because of the effects of strain. Recently Armelles, Rodriguse, and Briones[3] have measured the dielectric function of these SLS ($m=6$, $n=2,3,4$). To our knowledge, there have been no full-band-structure (FB) calculations of the dielectric function, $\vec{\vec{\epsilon}}(\omega)$, and second-harmonic generation (SHG) coefficient, $\vec{\vec{\chi}}^{(2)}(-2\omega;\omega,\omega)$, of these SLS, over a wide range of frequencies; Armelles, Rodriguse, and Briones[3] only give relative values of $\vec{\vec{\epsilon}}_2(\omega)$.

Here we report FB calculations of the dielectric function and SHG coefficient in strained $(GaAs)_n/(GaP)_n$ SLS on GaAs(001) substrates for $n=1,2$. We also study the effects of the strain on the size and the anisotropy of the optical response functions. For the full details of our approach for calculating electronic band structures and evaluating optical response functions, we refer the reader to the literature.[6-8] Here we only briefly describe our method.

To determine the lattice constants of these SLS, we employ a macroscopic elasticity theory (MET).[5,9,10] These values are summarized in Table I. To calculate the energy-band structure and momentum matrix elements, we use a minimal basis [18 orbitals ($1s,2s,2p,3s,3p,3d,4s,4p$) for Ga and As and 9 orbitals ($1s,2s,2p,3s,3p$) for P] linear combination of Gaussian orbitals (MLCGO) technique in conjunction with the $X\alpha$ method for constructing the potentials of the constituent bulk materials. The local single-site effective potentials and basis functions for bulk GaAs and GaP are constructed by adjusting the α's for bulk materials to produce the correct lowest bulk band gaps. We then use these *bulk* orbitals and potentials to construct the superlattice basis and effective potentials. Once the eigenvalues and eigenstates of the superlattice Hamiltonian are obtained, the momentum matrix elements are constructed. The values of $\vec{\vec{\epsilon}}_2(\omega)$ and $\vec{\vec{\chi}}^{(2)}(-2\omega;\omega,\omega)$ are then obtained by utilizing a linearized sampling method.

TABLE I. Lattice constants in Å. a_z is the lattice spacing in the z direction and $a_\parallel$ is the substrate lattice constant.

Substrate	$a_\parallel$	$a_z^{\text{Ga-As}}$	$a_z^{\text{Ga-P}}$
GaAs	5.654	1.413	1.316

This approach allows us to obtain a reasonably accurate band structure for the SLS without fitting to any of the superlattice properties. Furthermore, unlike in self-consistent local-density-approximation calculations, our band gaps are *not* underestimated. Our previous calculations of electronic and optical properties of $(Si)_n/(Ge)_n$ SLS (Ref. 6) are in good agreement with later self-consistent calculations and with experiment,[11] as are our calculations for $(GaAs)_n/(AlAs)_n$ SLS (Ref. 7) and pressure dependence of bulk semiconductors.[12-14] This indicates that, to a good approximation, the bulk orbitals and *single-site, atomiclike* potentials we use are indeed transferable to new geometries and materials. Furthermore, since the fitting that is done in the bulk calculations is at the basic level of the exchange-correlation potential, we feel the present approach is more fundamental than usual *ad hoc* empirical calculations.[15] Indeed, by iterating to self-consistency, it would become a first-principles calculation, although in its present *semi-ab-*

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initio form it is computationally more efficient than any first-principles calculation. This last point is a very important consideration in choosing a technique for calculating the frequency-dependent optical response, and in particular the *nonlinear* response, of materials that have a large number of atoms in the unit cell; such calculations involve evaluation of energy-band structure and momentum matrix at thousands of points throughout the irreducible segment of the Brillouin zone. On the other hand, one of the major deficiencies of the MLCGO approach is that, even though the overall frequency dependences of optical response functions are in general accurately predicted, the magnitude of the calculated response is, at worst, only within a factor of 2 of the actual value. Yet such calculations clearly indicate physical trends and can reasonably quickly identify interesting materials and structures which warrant future, more accurate calculations.

We present the results of our FB calculation of the imaginary part of the dielectric tensor, $\vec{\epsilon}_2(\omega)$, for $n=1,2$ in Fig. 1. The energy values of E_0 (direct band gap) from our calculations are given in Table II. In the same table, for $n=1$, we have also included the results of the *first-principles* calculation of the E_0 peak and its corresponding LDA-corrected value by Dandrea and Zunger (DZ).[4] As seen from Table II, there is good agreement between our result and the LDA-corrected value. Furthermore, in agreement with the results of DZ (Ref. 4) for GaAs (001) substrates, we find these SLS to have direct gaps in spite of the fact that GaP is an indirect-gap material.

In order to see the effect of the strain on the optical response function, we use an effective medium model (EMM) (Refs. 6 and 7) to calculate the $\vec{\epsilon}_2(\omega)$ in these SLS from the corresponding response of GaAs and GaP under tensile strain. First we obtain the $\vec{\epsilon}_2(\omega)$ for GaAs and strained (tensile) GaP from FB calculations (see Fig. 2). We then use the EMM to find the effective dielectric function of these SLS. These results are presented in Fig. 3. From comparing our microscopic results (Fig. 1) with that of the EMM [Fig. 3(a)], it is evident that the anisotropy is well reproduced by the EMM. Furthermore, when the EMM calculation is repeated with no strain in GaP [Fig. 3(b)], the anisotropy is drastically reduced, indicating that for the most part the anisotropy is due to the presence of the tensile strain in the GaP layers.

We would like to point out that in the case of the strained $(Si)_n/(Ge)_n$ SLS on Si(001) substrate, where the Ge is under compressive strain, we have found that at most frequencies $\epsilon_2^{zz}(\omega) > \epsilon_2^{xx}(\omega) = \epsilon_2^{yy}(\omega)$.[6] We have shown[6] that this arises, for the most part, from an alignment of more bonds along the SLS axis (z axis) than per-

TABLE II. Our theoretical values for direct band gaps in eV (E_0) along with the corresponding *first-principles* LDA results of DZ (Ref. 4). The values in parentheses are the LDA corrected results (Ref. 4).

n	1	2
Present	1.72	1.75
LDA	1.03 (1.78)	

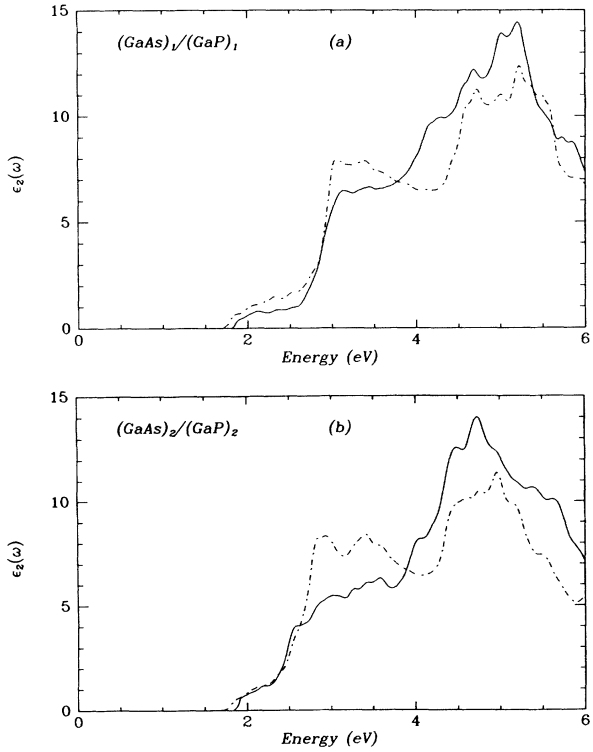

FIG. 1. $\vec{\epsilon}_2(\omega)$ for $n=1,2$ SLS [solid lines, $\epsilon_2^{xx}(\omega)=\epsilon_2^{yy}(\omega)$; dash-dotted lines, $\epsilon_2^{zz}(\omega)$].

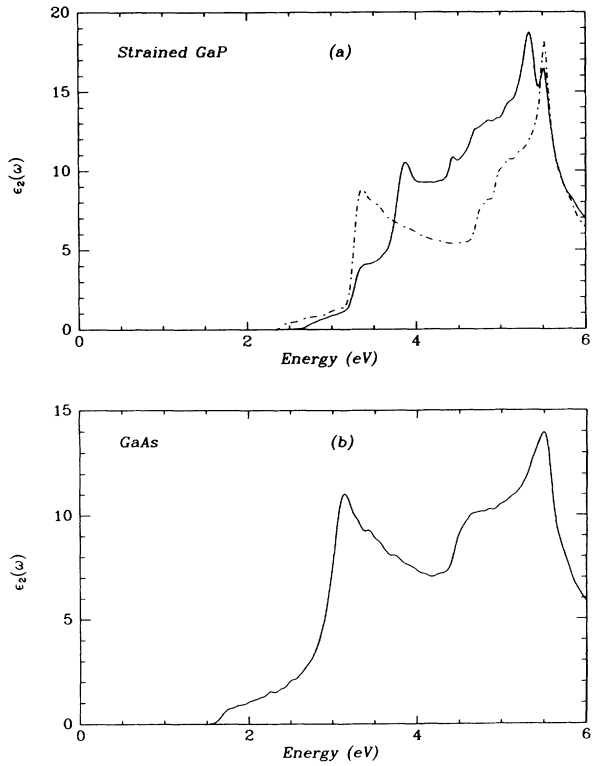

FIG. 2. $\vec{\epsilon}_2(\omega)$ for (a) strained GaP and (b) GaAs.

pendicular to it. In the present case, where the GaP layers are under tensile strain, the opposite is true. Therefore, it is not surprising that over most frequencies we find $\epsilon_2^{zz}(\omega) < \epsilon_2^{xx}(\omega) = \epsilon_2^{yy}(\omega)$.

Finally, a comparison of the microscopic and EMM results reveals that most of the prominent features of the response functions (such as the E_0 and E_1 peaks) arise from bulklike transitions, and that the effects of transitions from the zone folded states are small perturbations to these major features. This situation was indeed encountered in studying the response functions of the GaAs/AlAs SLS. However, these effects were too small to be detected in the actual measurements.[14] From the results of measurements of the $\vec{\epsilon}_2(\omega)$ (Ref. 3) of the strained $(GaAs)_m/(GaP)_n$ SLS, it is evident that this is also true for these SLS.

The results of our FB calculation of the magnitude of $\vec{\chi}^{(2)}(-2\omega;\omega,\omega)$ for $n=1,2$ SLS are presented in Fig. 4. The first major peak at around 0.9 eV is due to the 2ω resonance with the E_0 optical peak. The second major feature at around 1.5 eV is mostly due to the 2ω resonance with the E_1 optical peak. The dip at around 1.7 eV is due to the ω resonance with the E_0 peak. Finally, the large peaks and dips in the range of 2.0–2.5 eV are due to resonances with the E_2 peak. Our calculated values for $\vec{\chi}^{(2)}(0)$ for these SLS, along with the results from the EMM with and without strain,[7] and for bulk GaAs and GaP, are given in Table III. Note that for

TABLE III. Theoretical results for $\vec{\chi}^{(2)}(0)$ in units of 10^{-7} esu. The results from the EMM with strain are labeled by ST-EMM and with no strain by NS-EMM.

	$n=1$	$n=2$	NS-EMM	ST-EMM	GaAs	GaP
$\chi_{xyz}^{(2)}(0)$	2.0	2.4	1.6	1.9	2.5	1.0
$\chi_{zyx}^{(2)}(0)$	2.1	2.5	1.7	2.0	2.5	1.0

$\chi_{zyx}^{(2)}(0)$, the result of the EMM is simply equal to the average response of the constituent materials of the SLS, whereas for $\chi_{zyx}^{(2)}(0)$ it is given by Eq. (1) in Ref. 7.

From the results of Table III, it is evident that the size of the SHG in these SLS is considerably larger than the results of the EMM without strain. They are also larger than the corresponding results for the $(GaAs)_n/(AlAs)_n$ SLS.[7] This is because the structural properties of GaP and AlAs are very different, despite the fact that their band structures are fairly similar and their band gaps nearly equal. In particular, the tensile strain in the GaP layers, which is due to large lattice mismatch (3.7%) between GaP and GaAs, leads to considerable lowering of the direct gap of $(GaAs)_n/(GaP)_n$ SLS as compared with those of $(GaAs)_n/(AlAs)_n$ SLS. This in turn results in an enhancement of the SHG.

Finally, while the result of the EMM calculation with strain is much closer to the microscopic results than the result of the nonstrained EMM calculation, it still underestimates the response. Thus the enhancement of the SHG is not all due to the lowering of the effective band

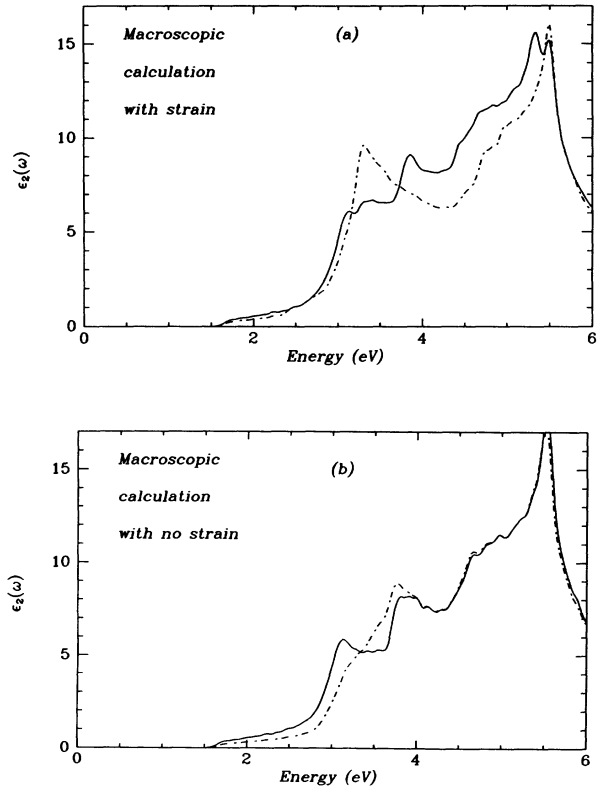

FIG. 3. $\vec{\epsilon}_2(\omega)$ from the EMM; (a) with strain, (b) without strain [solid lines, $\epsilon_2^{xx}(\omega)=\epsilon_x^{yy}(\omega)$; dash-dotted lines, $\epsilon_2^{zz}(\omega)$].

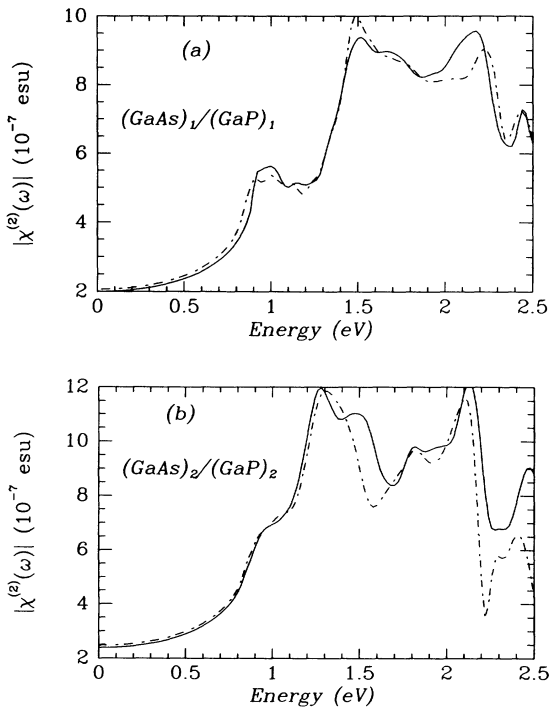

FIG. 4. $|\vec{\chi}^{(2)}(-2\omega;\omega,\omega)|$ for (a) $n=1,2$ SLS [solid lines, $\chi_{xyz}^{(2)}(\omega)$; crosses, $\chi_{zyx}^{(2)}(\omega)$].

gap under tensile strain. Part of the enhancement is also due to the presence of the large numbers of interfaces in the SLS,[8] an effect which cannot be accounted for by the EMM.

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