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Ab initio CALCULATIONS OF POLARIZATION, PIEZOELECTRIC CONSTANTS, AND ELASTIC CONSTANTS OF InAs AND InP IN THE WURTZITE PHASE

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We report first-principle density functional calculations of the spontaneous polarization, piezoelectric stress constants, and elastic constants for the III–V wurtzite structure semiconductors InAs and InP. Using the density functional theory implemented in the VASP code, we obtain polarization values -0.011 and -0.013 C/m^2, and piezoelectric constants e_{33} (e_{31}) equal to 0.091 (-0.026) and 0.012 (-0.081) C/m^2 for structurally relaxed InP and InAs respectively. These values are consistently smaller than those of nitrides. Therefore, we predict a smaller built-in electric field in such structures.

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1. INTRODUCTION

Despite significant advances achieved in Si photonics with based materials, the III–V compounds have superior optoelectronic properties and exhibit unique features (direct and tunable band gap) for light emission and detection. This represents some real advantages for optoelectronic functionalities (LEDs, lasers, photo detectors, photovoltaic) [1] to operate with high efficiency at various optical wavelengths. The integration of III–V materials in this field is based on epitaxial growth of nanowire. In recent years, much effort has been devoted to the growth and fabrication of strained InP/InAs/InP nanowire devices for the realization of high field-effect electron mobility transistors and circuits. Advantages of these systems include the high electron mobility and velocity of InAs and a large conduction band offset between InAs and InP (0.5 V) [2].

As is well known, when a nanowire heterostructure is epitaxially grown from materials with different lattice constants, an elastic strain field is created inside the material system [3]. This strain field can in general modify the electronic structure of the material system and can therefore be employed to tailor the electronic and optoelectronic properties of the nanowire heterostructure for applications. This strain can induce spontaneous polarization and piezoelectric fields with significant effects on the electronic and optoelectronic properties of the systems. Thus, it is in general of great importance to consider strain and piezoelectricity simultaneously when studying epitaxially grown strained nanowire heterostructures.

2. COMPUTATIONAL DETAILS

In this work, we calculate the spontaneous polarization, piezoelectric coefficients, and elastic constants of wurtzite structure InAs and InP using the generalized-gradient approximation (GGA) to density functional theory (DFT) as implemented in the VASP package [4]. The polarizations are obtained using the widely used Berry phase method [5], and the piezoelectric coefficients and elastic constants are obtained from the calculated dependence of polarization and energy on the appropriate strain. Ultrasoft potentials [4] are used for all atoms involved, and *d* semicore states are included in the valence for an In atom. The

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structural relaxation with strain perturbations is performed using the plane-wave projector augmented wave method (PAW) as implemented in the VASP code. We use the Heyd–Scuseria–Ernzerhof hybrid exchage-correlation functional [6] with the screening parameter $\mu = 0.2$ and the mixing parameter $\alpha = 0.25$ (HSE06). Indeed, this functional is well known to give accurate lattice parameters and band gaps in good agreement with experiment [7].

The results reported here are obtained with a plane-wave cutoff of 600 eV and a $6 \times 6 \times 4$ Monkhorst–Pack mesh [8] for Brillouin zone investigation; these parameters were found sufficient for the computed stress for systems considered to converge. Polarizations are reported relative to the conventional reference structure of the zinc blend structure with the same ratio of the c lattice constant to the unit cell volume [9], and care is taken to avoid problems associated with the branch dependence of the polarization by extracting the so-called proper piezoelectric response for the e_{13} coefficients [10].

3. POLARIZATION AND PIEZOELECTRIC EFFECTS

Typical bulk III–V compound semiconductors grow preferentially in the zinc blend (zb) phase. Bulk wurtzite (wz) crystals of III–V compound semiconductors are rare in nature (except for III-nitride materials). Nevertheless, it has been shown that it is possible to selectively grow thin III–V compound semiconductor nanowires in either the zinc blend or wurtzite phase, or in a superlattice form of these two phases. However, it is very challenging to experimentally establish the elastic and piezoelectric properties of wurtzite III–V compound semiconductors because of the lack of bulk wurtzite crystals of these materials in nature. Hence, theoretical calculation seems to be a good solution of such problems.

Before reporting our polarization results, we compare our HSE06 calculation of band structures of wz-InAs and wz-InP with those that we obtain using the generalized-gradient approximation (GGA) in the Perdew–Burke–Ernzerhof parameterization [11] (Fig. 1), at the calculated GGA lattice parameter. We find that the HSE06 calculated band gap for both wz-InAs (0.40 eV) and wz-InP (1.47 eV) is in good agreement with experimental values [12] (wz-InAs (0.52 eV) and wz-InP (1.49 eV)), whereas the GGA shows an underestimation of these values (Fig. 2). The "negative gap" of wz-InAs has already been observed in other calculations [13]. The main cause of this problem is the known limitation of the DFT-GGA to correctly describe excited-state properties like the band structure.

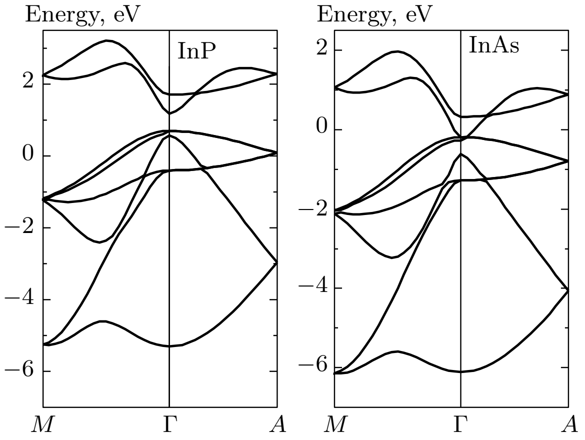

Fig. 1. Band structures of wz-InP and wz-InAs within GGA approaches at the calculated optimized GGA lattice parameters. Note that the GGA severely underestimates the band gap and results in a metallic ground state for wz-InAs

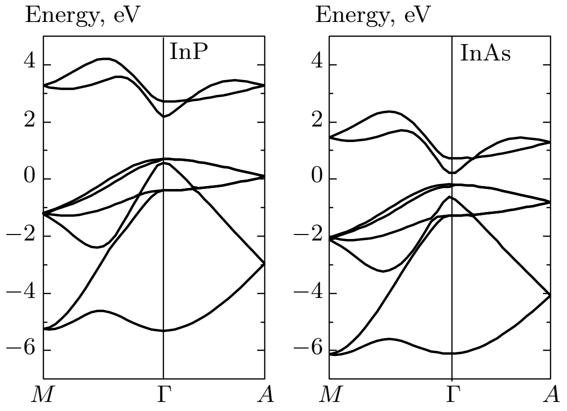

Fig. 2. Band structures of wz-InP and wz-InAs within HSE06 approaches at the calculated optimized GGA lattice parameters. We reproduce the correct gap with this hybrid functional

When a wurtzite structure semiconductor is constrained by epitaxial matching to a substrate or in a heterostructure, its total polarization is the sum of its intrinsic spontaneous polarization P_{sp} (the polarization that it would have in an unstrained bulk sample) plus the polarization induced as a result of the strain $P_{pz}(\varepsilon)$. The strain-induced component depends strongly on the strain ε and hence on the lattice mismatch between the epitaxial layers. In the linear regime, it is related to the piezoelectric tensor e as

$$P_{pz}(i) = \sum e_{ij}\varepsilon_j.$$

Both the intrinsic and strain-induced contributions can be calculated accurately from first-principle calculations [5, 14] and have been shown to be large in the III–V nitrides [15]. In the case of wurtzite symmetry, this tensor contains three independent elements P_x, P_y, and P_z. Thanks to intrinsic symmetry rules of the hexagonal lattice, many coefficients of the piezoelectric tensor are equal to zero, and only three coefficients are nonzero: e_{33}, e_{31}, and e_{15}.

$$[e_{ij}] = \begin{bmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{bmatrix}.$$

The coefficients e_{33} and e_{31} characterize polarization along the **z** axis (P_z), and e_{15} (shearing term) characterizes polarizations along **x** and **y** axis (P_x and P_y), which are in general neglected,

$$P_z = 2\left(e_{31} - \frac{c_{13}}{c_{33}} e_{33}\right)\varepsilon,$$

and C_{13} and C_{33} are the elastic constants. Hexagonal InAs and InP belonging to the point group 6mm show five independent elastic-stiffness coefficients: C_{11}, C_{12}, C_{13}, C_{33}, and C_{44}:

$$[C_{ij}] = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix}.$$

The coefficient C_{66} is related to C_{11} and C_{12} as $C_{66} = (C_{11} - C_{12})/2$.

4. RESULTS AND DISCUSSIONS

We begin by calculating the polarization and piezoelectric constants (e_{33} and e_{31}) at the calculated GGA equilibrium structures for InP ($a = 4.12$ Å, $c = 6.72$ Å, and $u = 0.3705$) and InAs ($a = 4.21$ Å, $c = 7.02$ Å, and $u = 0.3703$). Our results are reported in Table 1. For comparison, we also report these values for GaN, because we have not found results in literature to compare with both *wz*-InAs and *wz*-InP. This is how we verify the reliability of our simulations.

Table 1. Polarizations P and piezoelectric constants e_{33} and e_{31} for InP, InAs, and GaN calculated at the theoretical GGA equilibrium lattice parameters

	InP	InAs	GaN
e_{31}, C/m^2	−0.026	−0.081	−0.35
e_{33}, C/m^2	0.091	0.012	1.27
P, C/m^2	−0.011	−0.013	−0.029

Table 2. Elastic constants in GPa for wurtzite (*wz*) and zinc blend (*zb*) structures of InP and InAs calculated at the theoretical equilibrium lattice parameters and atomic positions

		C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
zb	InAs	80.3	43.3	–	–	36.9	–
	InP	98.4	45.4	–	–	39.5	–
wz	InAs	99.1	43.6	31.9	114.5	22.0	27.7
	InP	116.7	50.9	38.2	135.9	27.0	32.9

We note that, contrary to the gallium nitride [16], InP and InAs materials have very small polarization and piezoelectric coefficients. These values are mainly due to the low ionic character of the In–As and In–P binding. For the III-nitrides, the binding is highly ionic due to the large size of the nitrogen atom, which gives a large spontaneous polarization for nitrides. The piezoelectric effect is also related to the stress state of the material and the lattice mismatch. In fact, in the case of the InAs/InP system, the lattice mismatch is about 3 %, but it can reach 7 % in the case of nitrides (the InN/GaN system is an example), and that is why the *wz*-InAs and *wz*-InP piezoelectric constants are smaller than those of nitrides. The total polarization of respectively InAs and InP is about −0.08 C/mI and −0.03 C/mI. Consequently, a very low internal electric field magnitude is expected for InAs/InP quantum wires.

Finally, in Table 2, we report the elastic constants obtained by calculating the change in energy with strain for five different strain configurations. The details of the strain configurations used and the procedure for extracting the elastic constants are described in Ref. [15]. For comparison, we include the values of elastic constants in the cubic phase because we have no experimental results to compare with.

In the case of the zinc blend phase, the values of elastic constants are in good agreement with experimental ones [17], which was expected because the GGA describes the energetic properties of the ground state precisely. In the case of the wurtzite phase, we have no experimental data to compare with, but we expect our calculated values to be similarly appropriate.

5. CONCLUSION

In summary, we have calculated the spontaneous polarization, piezoelectric coefficients, and elastic constants for wurtzite structure InAs and InP. Since there is no experimental data until now for these materials, we have made a primary calculation for GaN, for which these parameters are well known. Then we provide our predictions for InAs and InP (which are experimentally inaccessible in the wurtzite structure). We find that, contrarily to nitride materials, our systems have smaller spontaneous polarization and piezoelectric coefficients. This explains the very small value of the internal electric field in wz-InAs and wz-InP.

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