Dielectric anisotropy of the GaP/Si(001) interface from first principles theory

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First principles calculations of the dielectric anisotropy of the GaP/Si(001) interface are compared to the anisotropy extracted from reflectance measurements on GaP thin films on Si(001) [O. Supplie et al. Phys. Rev. B 86 035308 (2012)]. Optical excitations from two states localized in several Si layers adjacent to the interface result in the observed anisotropy of the interface. The calculations show excellent agreement with experiment only for a charge compensated interface with a P layer in contact with Si thus demonstrating that a combination of theory and experiment can reveal localized electronic states and atomic structure at buried interfaces.

I. INTRODUCTION

Reflectance anisotropy (RA) is a long-established technique for probing optical transitions at surfaces of tetrahedral semiconductors, where the bulk cubic symmetry is broken via processes such as formation of surface dimers. In principle the technique can also be used to probe interfaces between dielectrics when the interface has an anisotropic optical response and the intervening layer is sufficiently translucent. However, interface optical anisotropy has only been measured in a few cases including: InP/GaAs(001) [1]; ZnSe/GaAs(001) and SiO2/Si(112) [2]; AlAs/GaAs(001) [3] and GaP/Si(001) [4–6]. Ellipsometric measurements have also been used to probe electronic behavior and charge transfer at the LaAlO3/SrTiO3 interface [7, 8] and at interfaces between high-k oxides and semiconductors [9, 10].

In this Letter we report first principles calculations of surface and interface dielectric anisotropies of thin GaP layers on Si(001) and compare them to experimental measurements of GaP films on Si(001) grown by metal oxide vapor phase epitaxy (MOVPE) by Supplie et al. [4]. Agreement between theory and experiment is excellent for charge compensated GaP layers where the last complete layer is P and is quite different when the last layer is Ga or the GaP thin film is not charge compensated. Charge compensation to produce a gapped interface is achieved by doping Si layers with Ga or P near the Si/GaP interface. Electron counting arguments given in Supplementary Material show that when the GaP surface is terminated by P dimers with one H atom per dimer, there is one electron more per dimer than is needed to satisfy valence requirements at the surface. This electron transfers to the GaP/Si interface and a gapped interface results when the Si layer is doped with one Ga(P) per surface dimer when the last GaP layer is P(Ga). Electrons transferred to the interface occupy localized states at the buried interface which are responsible for the observed interface dielectric anisotropy (IDA) [4].

Thus far there have been few calculations of optical interface anisotropies. Optical anisotropies of ZnSe/GaAs(001) [11] and AlAs/GaAs(001) [3] interfaces have been calculated using tight-binding electronic structure methods. The approach which is applied here was previously applied to systems including: clean Si and Ge(001) surfaces [12] and clean and transition metal covered Si(111) surfaces [13–15]. RA [4–6], low energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations [5, 16] have showed that GaP grown on Si(001) by MOVPE has a mixed (2x2) and c(4x2) P dimer surface. Dimers are tilted and have a H atom on the down-tilted P atom. This is supported by DFT calculations of surface energies of GaP(001) surfaces as a function of P and H chemical potential [17] which show that the GaP(001)-(2x2)H monohydride surface has the lowest formation energy at moderate P and H chemical potentials. Calculation of RA,

\[ \Delta r \over r = 2 r_x - r_y \over r_x + r_y, \]

where \( r_\alpha (\alpha = x, y) \) is the complex reflection coefficient along a particular axis, is usually performed for surfaces using dielectric functions for the bulk material and a slab terminated by the surface reconstruction of interest. These are used in a three-layer model proposed by McIntyre and Aspnes [18]. Yasuda [19] proposed a five-layer model (ambient, thin surface layer, thin film, thin interface layer and bulk medium, Fig. 1) to account for the RA of a thin film, of non-negligible thickness compared to the wavelength of light, \( \lambda \), on a bulk medium. It was developed further by Hunderi et al. [3] in 2005. According to this version of the five layer model, the RA can be expressed as [3, 4],

\[ \Delta r \over r = a(d_2, \lambda) d_1 \Delta \epsilon_1 + b(d_2, \lambda) d_3 \Delta \epsilon_3, \]

where

\[ a(d_2, \lambda) = 4 \pi i \over \lambda \over n_0 - \epsilon_2 \over n_0 - \epsilon_2 \left[ 1 - n_2 \over n_0 \right] c(d_2, \lambda), \]

\[ b(d_2, \lambda) = 4 \pi i \over \lambda \over n_2 \over n_2 - \epsilon_4 \over n_2 - \epsilon_4 \left[ 1 - n_2 \over n_0 \right] c(d_2, \lambda), \]

\[ c(d_2, \lambda) = r_{24} \over \over r_{02} \over r_{02} + r_{24} \over 2 \over (2), \]

\[ \Delta \epsilon_1 = \epsilon_{xx, i} - \epsilon_{yy, i}, \]

and

\[ \Delta \epsilon_3 = \epsilon_{xx, i} - \epsilon_{yy, i}. \]
$r_{ij}$ is the complex reflection coefficient for the interface between thick phases $i$ and $j$ (in this case: ambient and GaP thin film, $r_{02}$, GaP thin film and bulk Si, $r_{24}$) and $\beta_i = 2\pi n_i d_i / \lambda$ is a phase acquired by propagation through layer, $i$, of thickness, $d_i$, and complex refractive index, $n_i$. Multiple reflections at boundaries of the thin surface and interface layers are included in these coefficients. $d_1 \Delta \epsilon_1$ and $d_3 \Delta \epsilon_3$ are the surface dielectric anisotropy (SDA) and IDA, respectively. In this work, P dimer bonds are aligned with the $z$ direction.

According to Eq. 2, differences in reflection coefficient for either polarization of light in normal incidence depend on factors which contain only optical constants of thick layers ($i = 0, 2$ and $4$) and overlying film thickness, $d_2$, times differences in the dielectric functions of the thin layers [4]. Using pairs of RA measurements from a series of GaP thin films on Si(001) of differing thickness, Supplie et al. extracted the SDA and IDA and functions $a$ and $b$ in Eq. 2 [4, 6]. These extracted dielectric anisotropies are compared to results of hybrid DFT calculations presented below.

A GaP layer grown on an atomically flat Si(001) surface with a (2x2)H surface reconstruction above an integer number of Ga-P bilayers has one electron more per surface dimer than is needed for a saturated bond network (Supplementary Material). Excess electrons from surface dimers might be expected to exist in localized states at the surface. Alternatively, they could charge compensate holes created by replacing one Si atom per dimer in the Si layer by Ga. The valence band edge of Si(001) in contact with GaP lies 0.5 eV above the GaP valence band edge in our calculations, making Si layers adjacent to the interface a low energy reservoir for holes. Transfer of two electrons per (2x2) cell from the GaP surface to the interface in order to satisfy valence electron counting would generate an interface charge density of -0.5 Cm$^{-2}$ and an electric field strength of 2.9x10$^{10}$ Vm$^{-1}$ outside the interface charge layer. A field of this magnitude would generate a surface charge density of -2.6 Cm$^{-2}$ via linear response, assuming a susceptibility of $\chi = 10$ for the GaP thin layer. According to our hybrid DFT calculations, the surface does indeed become negatively charged, but to a lesser degree (-0.4 Cm$^{-2}$). The net charge on the P and H atom layer and on each Ga-P bilayer and several Si bilayers in the slabs used for compensated P/Si and Ga/Si interfaces is shown in Fig. 1. The negative charge, corresponding to about -1.5 e per (2x2) cell, is localized on the P dimers and first Ga-P bilayer. The interfaces carry a corresponding positive charge which mainly comes from depletion of charge on the Ga ions. The lower, pseudo-H atom terminated work (Supplementary Material). Excess electrons from surface dimers might be expected to exist in localized states at the surface. Alternatively, they could charge compensate holes created by replacing one Si atom per dimer in the Si layer by Ga. The valence band edge of Si(001) in contact with GaP lies 0.5 eV above the GaP valence band edge in our calculations, making Si layers adjacent to the interface a low energy reservoir for holes. Transfer of two electrons per (2x2) cell from the GaP surface to the interface in order to satisfy valence electron counting would generate an interface charge density of -0.5 Cm$^{-2}$ and an electric field strength of 2.9x10$^{10}$ Vm$^{-1}$ outside the interface charge layer. A field of this magnitude would generate a surface charge density of -2.6 Cm$^{-2}$ via linear response, assuming a susceptibility of $\chi = 10$ for the GaP thin layer. According to our hybrid DFT calculations, the surface does indeed become negatively charged, but to a lesser degree (-0.4 Cm$^{-2}$). The net charge on the P and H atom layer and on each Ga-P bilayer and several Si bilayers in the slabs used for compensated P/Si and Ga/Si interfaces is shown in Fig. 1. The negative charge, corresponding to about -1.5 e per (2x2) cell, is localized on the P dimers and first Ga-P bilayer. The interfaces carry a corresponding positive charge which mainly comes from depletion of charge on the Ga ions. The lower, pseudo-H atom terminated work (Supplementary Material). Excess electrons from surface dimers might be expected to exist in localized states at the surface. Alternatively, they could charge compensate holes created by replacing one Si atom per dimer in the Si layer by Ga. The valence band edge of Si(001) in contact with GaP lies 0.5 eV above the GaP valence band edge in our calculations, making Si layers adjacent to the interface a low energy reservoir for holes. Transfer of two electrons per (2x2) cell from the GaP surface to the interface in order to satisfy valence electron counting would generate an interface charge density of -0.5 Cm$^{-2}$ and an electric field strength of 2.9x10$^{10}$ Vm$^{-1}$ outside the interface charge layer. A field of this magnitude would generate a surface charge density of -2.6 Cm$^{-2}$ via linear response, assuming a susceptibility of $\chi = 10$ for the GaP thin layer. According to our hybrid DFT calculations, the surface does indeed become negatively charged, but to a lesser degree (-0.4 Cm$^{-2}$). The net charge on the P and H atom layer and on each Ga-P bilayer and several Si bilayers in the slabs used for compensated P/Si and Ga/Si interfaces is shown in Fig. 1. The negative charge, corresponding to about -1.5 e per (2x2) cell, is localized on the P dimers and first Ga-P bilayer. The interfaces carry a corresponding positive charge which mainly comes from depletion of charge on the Ga ions. The lower, pseudo-H atom terminated...
Si surface carries close to zero net charge. Depletion of charge from the interface results in layer expansion at the interface. Removal of the lowest P layer to form a sharp Ga/Si interface creates four holes at the interface, which are filled by transfer of two excess electrons per (2×2) cell from the surface and replacing two atoms in the Si layer by P. Hence a compensated Ga/Si interface also requires transfer of two electrons from the surface to the interface. The net charge on each bilayer for the compensated surfaces is essentially identical. The net charge at the P/Si and Ga/Si compensated interfaces is the same, but the charge distribution over bilayers (Fig. 1) and their IDA differ.

The electronic structure of the slab used for hybrid DFT calculations, projected onto four atomic layers at the compensated P/Si interface, is shown in Fig. 2. There are two occupied interface localized states which lie above the GaP layer valence band maximum throughout most of the Brillouin zone. Moduli squared for these states at the \( \Gamma \) and \( \tilde{\Gamma} \) points of the Brillouin zone are also shown in Fig. 2. The lower energy interface state at \( \tilde{\Gamma} \) (labelled \( \Gamma_1 \)) is strongly localized in the Si layer which contains two Ga dopants and the Si bilayer immediately beneath. The higher energy interface state at \( \tilde{\Gamma} \) (labelled \( \Gamma_2 \)) extends two Si bilayers further from the interface. At \( \tilde{\Gamma} \) where the interface states are quasi-degenerate, there is an intermediate degree of localization and the state penetrates some way into the GaP layer.

Two interface states with similar localization and dispersion to those just described for the compensated P/Si interface are found at the compensated Ga/Si interface (Supplementary Material, Fig. 4). Compensated P/Si and Ga/Si interfaces have two Si atoms replaced by either Ga or P. Further calculations were performed in which these atoms were successively replaced by Si leaving one or two electrons (P/Si) or holes (Ga/Si) in either slab. Electrons in the P/Si slab become localized on atoms in the layer which contained compensating Ga atoms. A band becomes half-filled when both Ga are replaced by Si to yield an abrupt P/Si interface and the Fermi level shifts above 1 eV above the GaP valence band maximum. Holes in the slab with the Ga/Si interface localize in the interface states in the Si layers described above.

The CRYSTAL program [20] was used to obtain relaxed atomic coordinates and their electronic structures. The hybrid DFT method used to calculate surface and interface dielectric anisotropies in this work has been described elsewhere [12]. The expression used to calculate dielectric functions in Eq. 2 contains the electron momentum operator, which is expressed in a local orbital basis. A filter function is applied to momentum operator matrix elements which selects contributions to slab dielectric functions from initial state wavefunctions in surface or interface regions. Similar approaches have been applied previously for this purpose [21, 22] and the method used here is described in Supplementary Material. The overall effect of these filters (Fig. 1) is to turn off contributions to dielectric functions from parts of initial state wave functions which lie outside them.

FIG. 3: (Color online) (Upper panel) Interface dielectric functions of compensated P/Si and Ga/Si interfaces with the incident radiation electric vector aligned parallel or perpendicular to the P dimer bond (solid and dotted curves, respectively). (Lower panel) IDA calculated for compensated P/Si and Ga/Si interfaces using filter functions of width 3 Si + 3 GaP bilayers (solid curves), 3 Si bilayers (dashed curve) and experiment redrawn from Ref. [4].

Imaginary parts of interface dielectric functions in layer 3, \( \text{Im}(\epsilon_{xx,3}) \) or \( \text{Im}(\epsilon_{yy,3}) \), times layer thickness, \( d_3 \), for normal incidence radiation are shown in the top panels of Fig. 3. \( \epsilon_{xx,3} \) is calculated with the electric vector polarized parallel to surface dimers (and atomic rows in the lowest complete Ga-P bilayer). \( \epsilon_{yy,3} \) is calculated with the electric vector polarized perpendicular to dimers. The IDA is the difference in these functions, \( d_3 \Delta \epsilon_3 = d_3(\epsilon_{xx,3} - \epsilon_{yy,3}) \). Interface dielectric functions and IDA for compensated P/Si and Ga/Si interfaces are shown in the lower panels of Fig. 3. IDA functions for both types of interface show similar curves, with a crossover from positive to negative IDA above 3 eV, but the agreement between the compensated P/Si interface and experiment in the lower left panel is clearly much better. The first layer deposited in MOVPE of GaP on Si(001) was P in the IDA data shown [4].

In order to determine the region from which the IDA originates, IDA spectra were compared with the filter function extending from three Si bilayers below the bottom P layer to 3 Ga-P bilayers above the bottom P layer (solid blue line) and where the filter function has the same lower limit in Si to the bottom P layer (dashed red line), eliminating any IDA contribution from GaP. Comparison to the experimental data (dotted line) shows excellent agreement with experiment for the compensated P/Si interface. Anisotropy arises in the Si bilayers adja-

\[ \Delta \epsilon_{xx} = \frac{1}{d_3} \int_{-d_3}^{d_3} \Delta \epsilon(x) \, dx \]

\[ \Delta \epsilon_{yy} = \frac{1}{d_3} \int_{-d_3}^{d_3} \Delta \epsilon(y) \, dy \]
cent to the GaP because when the filter excludes the GaP layer (red dashed lines), almost all of the IDA is retained, compared to when the GaP layer is included (solid blue line). The shape of the positive peak below 3 eV and the strong dip at 3.5 eV are reproduced. In contrast, the positive peak for the compensated Ga/Si interface is shifted to lower energy than the experimental peak and the dip at 3.5 eV and extra peak at 4.0 eV are not reproduced. IDA functions for compensated, gapped interfaces and uncompensated interfaces with electrons or holes localized at interfaces are compared to experimental data in Supplementary Material. Ungapped interfaces have IDA which are not in agreement with experiment, showing that the interfaces reported by Supplie et al. were gapped [4].

Finally, optical transitions which are responsible for the observed IDA signal are identified by inspecting the strongest transitions in energy windows centered at 3.0 and 3.5 eV with widths of 0.2 eV. These windows are located at the positive peak and the negative dip in the compensated P/Si IDA spectrum (Fig. 3 bottom left). Strengths of optical transitions at a given photon energy, $E$, with the electric field vector along direction $\alpha$ are determined by moduli squared of momentum matrix elements and transition energies, $|p_{n\alpha k}|^2 \delta(E - E_{nn\alpha k})$. $n$ and $n'$ are initial and final state labels at k point $k$ and $E_{nn\alpha k}$ is an interband transition energy. The strongest optical transitions at 3.0 eV for a compensated P/Si interface with the electric vector aligned with the $x$ direction, occur between initial states which are the occupied interface state which is highest in energy and vacant interface-localized states along the $\Gamma J$ edge of the Brillouin zone (Fig. 2). The dip at 3.5 eV arises from transitions from interface states with $k$ vectors lying along another edge of the Brillouin zone ($\Gamma J$) and the electric field aligned with the $y$ direction. These transitions occur at higher energy (3.5 eV) because of the downwards dispersion of the interface states along $\Gamma J$. Transitions from interface-localized initial states in other parts of the Brillouin zone are much weaker. Hence the dielectric anisotropy at the GaP/Si(001) interface arises from localized states in Si bilayers adjacent to the GaP thin layer and the main contributions come from states along high symmetry directions in the Brillouin zone.

In summary, electron counting using conventional ideas about valence at the GaP/Si(001) surface and interface shows that the number of electrons in the P dimer layer is too large by one per dimer. A compensated, gapped surface and interface are achieved by replacing one Si per dimer by a Ga for a P terminated GaP layer or by replacing one Si per dimer by a P for a Ga terminated GaP layer. Transfer of electrons from surface to interface results in a large, negative areal charge density at the interface. Linear response of the GaP layer to the negative layer results in reversal of the net charge transfer and net negative/positive surface/interface layers. Electrons transferred to the interface are trapped within three Si bilayers closest to the GaP layer. Optical transitions of these trapped electrons at compensated, gapped P/Si interfaces result in the experimentally observed IDA. Uncompensated, unconfined or gapped Ga/Si interfaces result in IDA not in agreement with experiment.

A combination of measurement and theoretical calculation can therefore be used to determine the layers in contact at the interface and the gapped or ungapped character of interface electrons.

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Supplemental Material for Dielectric anisotropy of the GaP/Si(001) interface

I. INFORMATION IN THIS DOCUMENT

This document contains Sections which describe: electron counting used to account for the electronic structures found at compensated and uncompensated P/Si and Ga/Si interfaces in hybrid DFT calculations as well as the GaP/Si(001)-(2x2)H surface; methods used to calculate surface and interface dielectric functions of slabs used in this work and details of electronic structure calculations.

II. ELECTRONIC STRUCTURE

A. Electron counting

Bulk GaP bilayers with a (001) surface orientation have eight valence electrons per Ga-P atom pair which can be distributed so that Ga-P bonds within each bilayer are saturated and each bilayer has one electron available for bonding to layers above and below the bilayer (Fig. 1, upper diagram). Formation of P dimers at a GaP(001) surface requires ten electrons from P dimer atoms - four for backbonds to the top Ga layer, four for P lone pairs and two for the P dimer bond - and is electronically saturated.

![Figure 1](image)

Addition of one H atom to each P dimer in the (2x2)H reconstruction results in one excess electron per P dimer over and above a saturated bond network (Fig. 1, bottom panel). A GaP layer grown on an atomically flat Si(001) surface with a (2x2)H surface reconstruction and a sharp P/Si interface therefore has one electron more per surface dimer than is needed for a saturated bond network. The Si bulk valence band edge lies 0.5 eV above the GaP bulk valence band edge in our hybrid DFT calculations, which may be compared to a value of 0.78 eV in the work of Supplie et al. [1]. Excess electrons or holes are accommodated in Si layers at the Si/GaP interface since the Si valence and conduction bands lie within the GaP band gap. This is indeed the case in hybrid DFT calculations where abrupt GaP/Si interfaces have excess electrons or holes localized at the interface for P/Si or Ga/Si interfaces (See Section II C). The abrupt P/Si interface has two interface localized electrons per (2x2) unit cell and the abrupt Ga/Si interface has two interface localized holes, using the electron counting described above. Gapped P/Si or Ga/Si interfaces only exist therefore when the Si layer is doped to compensate these electrons or holes with two Ga or two P per (2x2) cell.

The notation P/Si + nGa replaceSi is used to refer to a P/Si interface with n Ga atoms replacing Si atoms in the layer below. The mixed Si/Ga layer contains two Si and two Ga atoms. P/Si + 1Ga replaceSi and P/Si + 0Ga replaceSi interfaces contain one and two excess electrons, respectively, and are not expected to be gapped. When the last GaP bulk layer GaP/Si(001) interface is Ga, then the uncompensated interface has two excess holes per (2x2) cell. The notation used in this case for an interface with m compensating P atoms replacing Si atoms in the layer beneath is Ga/Si + mP replaceSi.

![Figure 1](image)

B. Surface electronic structure

The electronic structure of the GaP/Si(001)-(2x2)H structure projected onto atoms in the P dimer and top Ga and P bulk layers is shown in Fig. 2. Surface atom projections for compensated P/Si + 2Ga replaceSi and uncompensated P/Si interfaces and Ga/Si interfaces are very similar, indicating that the surface and interface electronic structures are independent for the GaP layer thickness chosen. There are two surface state bands localized on P dimer atoms. The lowest unoccupied states at the surface are localized on Ga atoms bonded to the P dimer atoms. Surface state dispersion is similar to that recently reported for this system by Romanyuk et al. [1].
C. Interface electronic structure

Fig. 3 shows projections of electronic states for compensated and uncompensated P/Si interfaces on four layers of atoms at the interface (labeled in the left panel of Fig. 1 in the main text). The P/Si + 2Ga$_{Si}$ is gapped and shows the pair of states at the Si/GaP interface localized in the Si layers closest to GaP which were discussed in the main text. The P/Si + 1Ga$_{Si}$ and P/Si + 0Ga$_{Si}$ uncompensated interfaces one and two electrons localized in interface states at mid gap. One or two states become half-filled when these states are present and they markedly change the predicted IDA (see Section III C).

Fig. 4 shows projections of electronic states for compensated and uncompensated Ga/Si interfaces on four layers of atoms at the interface (labeled on the right panel of Fig. 1 in the main text). The compensated Ga/Si +
2P$_{Si}$ is gapped. In the uncompensated Ga/Si interfaces there are one or two holes present at the interface. One or both of the interface states which are filled in the compensated Ga/Si interface become half empty when these holes are present. The number and interface localization of the holes and electrons for Ga/Si and P/Si interfaces is exactly what one would predict on the basis of electron counting and transfer of two electrons from the surface dimers to the interface in Section II A. Dispersion of interface states is in reasonable agreement with states found by Romanyuk et al. in Ref. [1].

III. FIRST PRINCIPLES CALCULATIONS OF OPTICAL ANISOTROPIES

A. Method of calculation

The dielectric susceptibility of bulk or slab structures used in calculations is,

$$\chi_{\alpha\alpha}(\omega) = \frac{2\varepsilon^2}{m^2\varepsilon_0\omega^2} \sum_{mn'k} \frac{(f_0(E_{nk}) - f_0(E_{n'k}))(p_{nn'k})^2}{(E_{nn'k} - E - i\delta)},$$

(1)

where $f_0$ is a Fermi occupation factor, $p_{nn'k}$ is a momentum matrix element connecting states $n\mathbf{k}$ and $n'\mathbf{k}$ in the presence of an electric field along direction $\alpha$, $E_{nn'k}$ is the corresponding transition energy and $m$, $e$ and $\Omega$ are the electron mass, charge and unit cell volume (or area for slab calculations). The bulk susceptibility is dimensionless and the surface susceptibility has dimensions of length since the unit cell volume in the denominator of the bulk susceptibility is replaced by the surface unit cell area in a surface or interface susceptibility of finite width.

The surface RA expression derived for a three layer model [2],

$$\frac{\Delta r}{r} = \frac{4\pi i n_0}{\lambda} \Delta \epsilon_1,$$

(2)

is retrieved by setting the interface reflection coefficient, $r_{24}$, to zero in Eq. 2 in the main text.

In order to select contributions to the dielectric function from particular layers in a slab, momentum matrix elements in the Gaussian atomic orbital basis used in this work were multiplied by a filter function,

$$f(z) = \frac{1}{2} \left( \tanh\left(\frac{z - z_1}{z_0}\right) - \tanh\left(\frac{z - z_2}{z_0}\right) \right),$$

(3)

which takes the value 1 for $z_1 < z < z_2$ and goes smoothly to zero outside this range. The value of $z_0$ was chosen to be 1 bohr radius. Modified momentum matrix elements scaled by the filter function are given by,

$$p_{nn'k} f(R_{j,z}) = \frac{\hbar}{i} \langle \Psi_{n'k} | \nabla | \Psi_{nk} \rangle f(R_{j,z})$$

$$= \frac{\hbar}{i} \sum_{i,j} c_{i,n'k} c_{j,nk} \langle \phi_i(r - R_i) | \nabla | \phi_j(r - R_j) \rangle f(R_{j,z}),$$

where $R_i$ and $R_j$ are position vectors of atomic sites where basis functions $\phi_i$ and $\phi_j$ are located, $R_{j,z}$ is the cartesian $z$ component of the vector $R_j$ and $c_{i,n'k}$ and $c_{j,nk}$ are expansion coefficients of the empty and occupied Bloch states, $\Psi_{n'k}$ and $\Psi_{nk}$, at wavevector $\mathbf{k}$. Multiplying the momentum matrix element, $p_{nn'k}$, by the filter function, $f$, selects contributions to the dielectric function from layers in a slab which lie between $z_1$ and $z_2$.

B. GaP/Si(001) SDA and RA

From their analysis of reflectance anisotropy (RA) spectra of pairs of GaP thin films on Si(001), Supplie et al. extracted the imaginary part of the surface dielectric anisotropy (SDA) (Ref. [3], Fig. 4). The SDA ($d_1\Delta\epsilon_1$) is reproduced in Fig. 5 where it is compared to results from this work. Overall, the peaks and dips obtained using a filter function extending four Ga-P bilayers into the GaP thin film are in reasonable agreement with experimental SDA although the first computed dip and peak are shifted down compared to experiment by about 0.4 eV. Similar relative shifts of calculated and experimental RA spectra to lower energy using this approach have been observed for clean Si surface states [4]. This shift is not found for interface states and is attributed to reduced screening of the Fock exchange potential at surfaces owing to lower electron densities there. The hybrid DFT approach used here has a fixed weight for the Fock potential which is the same for both the bulk interface and the surface and therefore does not take into account any difference of screening at the surface, bulk or interface.

Surface reflectance anisotropy (RA) spectra (Eq. 2) calculated for slabs with the GaP/Si(001)-(2x2)H surface and compensated and uncompensated interfaces are shown in Fig. 6. RA spectra (Eq. 2) are closely related...
FIG. 5: (Color online) SDA spectra of the GaP/Si(001)-(2x2)H surface reconstruction with a compensated P/Si + 2Ga interface compared to experimental SDA spectra redrawn from Ref. [3]. Computed SDA spectra are shown for surface dielectric function contributions down to the first two or four Ga-P bilayers.

FIG. 6: (Color online) RA spectra of the GaP/Si(001)-(2x2)H surface reconstruction with compensated and uncompensated P/Si and Ga/Si interfaces compared to experimental RA spectra redrawn from Ref. [3]. A filter function Eq. 3 was used to select contributions to the IDA which arise from transitions with initial states in the three Si bilayers and three GaP bilayers which are closest to the interface.

FIG. 7: (Color online) IDA for the GaP/Si(001) interface from theory (solid curves) and experimental data (dotted curves) redrawn from Ref. [3]. A filter function Eq. 3 was used to select contributions to the IDA which arise from transitions with initial states in the three Si bilayers and three GaP bilayers which are closest to the interface.

ID spectra calculated for P/Si and Ga/Si interfaces with various degrees of compensation by Ga and P substitution of Si are compared to experimental IDA data of Supplie et al. [3] in Fig. 7. The experimental data shows a positive IDA with a broad peak around 3 eV and a dip at 3.5 eV. A second, narrow peak is found at 3.7 eV. Each of the P/Si interfaces studied shows a positive IDA rising to a maximum around 3 eV. Uncompensated and partially compensated P/Si + 0GaSi or 1GaSi interfaces have a small positive IDA below 2 eV owing to SDA spectra ($d_1\Delta\epsilon_1$). The former contain a denominator factor of $(\epsilon_0 - \epsilon_2)$, the difference in ambient and thin surface layer dielectric functions. In order to compare shapes of experimental and computed RA spectra, the latter were shifted to higher energy by 0.4 eV. RA spectra are essentially converged after four bilayers are included, except in the region around 3.0 eV. The overall shape of the experimental spectrum is reproduced quite well.
optical transitions from occupied interface states at mid-gap. Only the fully compensated P/Si + 2Ga_{Si} interface shows the narrow positive peak which occurs at 3.7 eV in experiment.

The fully compensated Ga/Si + 2P_{Si} interface has a positive IDA with a peak around 2.9 eV. It switches to negative above 3 eV but does not show the sharp, positive peak found in the P/Si fully compensated interface. Ga/Si + 0P_{Si} or 1P_{Si} interfaces have one or two holes localized at the interface and partly occupied interface states in the GaP bulk band gap. They have a positive IDA below 3 eV but do not show the positive peak just above 3 eV which is found in experiment. Changes in the IDA induced by filled or empty states at mid-gap for uncompensated P/Si or Ga/Si interfaces mean that there is little agreement with experiment when the interface is not compensated. Thus IDA measurements may be a good means of determining whether an interface is gapped or not. It is worth noting that the H covered Si(001) interface work of Supplie et al. is first exposed to tri-butyl phosphine and it is believed that the Si substrate is covered by P. A series of calculations of GaP/Si(001) interface formation energies by Romanyuk et al. [1] found that the P/Si + 2Ga_{Si} interface had the lowest formation energy.

IV. DETAILS OF ELECTRONIC STRUCTURE CALCULATIONS

The GaP/Si(001) system was modeled using slabs containing six GaP bilayers and five Si bilayers with GaP layers terminated by P dimers and Si layers terminated by pseudo H atoms. The IDA of a thicker slab containing six GaP bilayers and ten Si bilayers was used to confirm that results had converged for the thinner slabs.

Gaussian orbital basis sets were used to expand wave functions in hybrid density functional theory (DFT) calculations. Basis sets for Ga, P, Si and H are described in Refs. [5], [6], [7] and [8], respectively. Published Ga and P basis sets were supplemented with additional sp shells with exponents 0.075 and 0.23, respectively. ECP18MWB and ECP10MWB pseudopotentials used for Ga and Si are described in Refs. [9] and [10]. The Ga pseudopotential contained 21 pseudized core electrons and 3d and higher lying valence states were explicitly included in wavefunction expansions. Core orbitals in the all-electron basis sets used for Ga and Si were omitted since core electrons in these atoms were treated using pseudopotentials. All atoms in the slab except the bottom layer of Si and the hydrogen layer were allowed to relax during energy minimization calculations.

The hybrid DFT functional used in this work was a modified version of the B3LYP functional [11] in which the weight of Fock (exact) exchange was reduced from 0.2 to 0.05 in order to obtain improved agreement between the calculated and experimental dielectric functions of bulk Si. The weight of Fock exchange was adjusted so that the E1 and E2 peaks in the computed dielectric function of bulk Si agree as well as possible with experiment. Hence no upwards shift of the empty state band structure is employed. The weight of Fock exchange which gives optimal agreement between theory and experiment for bulk Si also results in good agreement between the computed and experimental dielectric functions of bulk GaP. Further details of this approach are given in Ref. [4].

All self-consistent field calculations were performed using the Crystal program [12] with a 6 x 6 Monkhorst-Pack grid [13] for surface Brillouin zone integration. Surface and bulk dielectric functions were calculated using the Exciton code [14]. Integration over the Brillouin zone in dielectric function calculations was performed using an interpolation method. A 24 x 24 x 24 Monkhorst-Pack grid [13] was used for Si and GaP bulk dielectric function calculations. Dielectric functions for GaP/Si(001)- (2x2)H slabs with were calculated using 16 x 16 grids and an interpolation technique equivalent to the tetrahedron method for bulk solids.