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 [O. Supplie et al., Phys. Rev. B 86 035308 (2012)]. The surface layer contains P dimers with one H atom. Each dimer transfers an electron to the interface producing a pair of states localized in the Si layers in contact with GaP. Optical excitations from these states result in the observed dielectric anisotropy of the interface.

The calculations show excellent agreement with experiment for a charge compensated interface with a P layer in contact with Si demonstrating that this combination of theory and experiment can probe electronic states localized at 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. In practice, however, interface optical anisotropy has only been measured in a few cases including: InP/GaAs(001) [1]; ZnSe/GaAs(001) and SiO$_2$/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 LaAlO$_3$/SrTiO$_3$ 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 Information show that when the GaP surface is terminated by P dimers with one H atom per dimer in a (2x2) surface unit cell, 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). Transfers electrons to the interface occupy localized states at the interface which are responsible for the observed interface dielectric anisotropy (IDA) [4]. Combined optical experiments and theory offer an important probe of interface conductivity and electronic states in many systems of current interest.

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 a range of 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,

$$\frac{\Delta r}{r} = \frac{2r_x - r_y}{r_x + r_y},$$

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],

$$\frac{\Delta r}{r} = a(d_2, \lambda)d_1 \Delta \epsilon_1 + b(d_2, \lambda)d_3 \Delta \epsilon_3,$$

where,

$$\Delta \epsilon_i = \epsilon_{xx,i} - \epsilon_{yy,i}$$
\begin{align*}
a(d_2, \lambda) &= 4\pi i \frac{n_0}{\lambda} \frac{1}{\epsilon_0 - \epsilon_2} \left[ 1 - \frac{n_2}{n_0} c(d_2, \lambda) \right], \\
b(d_2, \lambda) &= 4\pi i \frac{n_2}{\lambda} \frac{1}{\epsilon_2 - \epsilon_4} c(d_2, \lambda), \\
c(d_2, \lambda) &= r_{24} \frac{1 - r_{02}^2}{(r_{02} + r_{24}e^{2i\beta_2})(1 + r_{02}r_{24}e^{2i\beta_2})}.
\end{align*}

FIG. 1: (Color online) Five layer model (left panel) and structures of (2x2) slabs (right panel) with GaP layer terminated by Ga or P and compensated by mixed P/Si or Ga/Si layers. Layers 0 to 4 are marked on the five layer model and envelope functions used to select optical transitions are shown. Layer 2 is the GaP thin film layer and is not shown to scale. Small spheres are H atoms, medium sized red spheres are P atoms, large green spheres are Ga atoms and medium sized grey spheres are Si atoms.

Supplie et al. extracted the SDA and IDA and functions \( a \) and \( b \) in Eq. 3 \([4, 6]\). 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 Information). 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 0.4 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 \(-0.5 \text{ Cm}^{-2}\) and an electric field strength of \(1.1 \times 10^{11} \text{ Vm}^{-1}\) outside the interface charge layer. A field of this magnitude would generate a surface charge density of -
10 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 (-7.5 Cm\(^{-2}\)). The net charge on the P and H dimer 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 (2x2) 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 \(\bar{\Gamma}\) points of the Brillouin zone are also shown in Fig. 2. The lower energy interface state at \(\bar{\Gamma}\) is strongly localized in the Si layer which contains two Ga dopants and the Si bilayer immediately beneath. The higher energy interface state at \(\bar{\Gamma}\) extends two Si bilayers further from the interface. At \(\bar{\Gamma}\) 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 Information, Fig. 2). 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 and 3 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 Information. The overall effect of the filter is to turn off contributions to the dielectric function from parts of initial state wavefunctions which lie outside the window.

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].
face 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 and that the anisotropy arises in the Si bilayers adjacent to the GaP. 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 Information. 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, $|p_{nm\alpha}^{\Gamma J}|^2 S(E - E_{nm\alpha})$. $n$ and $n'$ are initial and final state labels at $k$ point $k$ and $E_{nm\alpha}$ 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 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. A simple calculation of the magnitude of this linear response yields an answer in reasonable agreement with the net charges of 1.5 e found in hybrid DFT calculations. 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, ungapped interfaces 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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