Second-harmonic generation as a probe for structural and electronic properties of buried GaP/Si(001) interfaces

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Abstract

Optical second-harmonic generation is demonstrated to be a sensitive probe of the buried interface between the lattice-matched semiconductors gallium phosphide and silicon with (001) orientation. Ex situ rotational anisotropy measurements on GaP/Si heterostructures show a strong isotropic component of the second-harmonic response not present for pure Si(001) or GaP(001). The strength of the overlaying anisotropic response directly correlates with the quality of the interface as determined by atomically resolved scanning transmission electron microscopy. Systematic comparison of samples fabricated under different growth conditions in metal–organic vapor phase epitaxy reveals that the anisotropy for different polarization combinations can be used as a selective fingerprint for the occurrence of anti-phase domains and twins. This all-optical technique can be applied as an in situ and non-invasive monitor even during growth.

Keywords: second-harmonic generation, internal interface, nonlinear optics, rotational anisotropy SHG, metal–organic vapor phase epitaxy, scanning transmission electron microscopy, GaP/Si(001) heterostructure

(Some figures may appear in colour only in the online journal)
nonpolar semiconductor and which promises many optoelectronic applications based on silicon electronics [8–13]. This system is of particular interest because the lattice mismatch between GaP(001) and Si(001) is small. Therefore, strain induced defects can be neglected. Nevertheless, the heteroepitaxial growth is challenging because the interface is not automatically charge neutral and anti-phase domains (APDs) can be formed at monoatomic steps of the substrate [14, 15]. Moreover, stacking faults and twins can be formed in the GaP film. The latter occur if a part of the crystal is rotated with respect to the main crystal orientation. The structure of these defects has been extensively investigated by means of STEM [16–18]. In order to optimize the conditions for a defect-free growth, however, an in situ technique for the evaluation of the interface quality during growth would represent a great progress towards an detailed understanding of the interface formation and for the preparation of highly efficient devices.

Here, we show that SHG is able to non-invasively investigate the properties of the buried interface between GaP and Si and that it is possible to directly relate the SHG anisotropy to the interface quality. For this purpose we have prepared GaP/Si samples by metal–organic vapor phase epitaxy (MOVPE) under different growth conditions that give rise to specific defects such as APDs or twins. We present sets of the rotational anisotropy of the second-harmonic intensity for different polarization combinations of the incoming fundamental and generated second harmonic in reflection and compare these results with atomically resolved STEM measurements. The combination of both experimental techniques allows us to identify the occurrence of specific defects in the second-harmonic anisotropy for particular polarization combinations. This makes it feasible to use second-harmonic anisotropy as an in situ, non-invasive probe for the interface quality even during growth. It would be complementary to other optical techniques like reflection anisotropy spectroscopy which is particularly used to monitor the surface properties under growth conditions in a MOVPE reactor [19].

The experiments were performed under ambient conditions using 50 fs laser pulses generated by a femtosecond Ti:Sapphire laser amplifier system operating at 800nm at a repetition rate of 15 kHz. The linear polarized laser beam at fundamental frequency $\omega$ was focussed under an angle of 45° onto the sample as illustrated in figure 1(a). The generated second-harmonic light at frequency $2\omega$ was observed in reflection for a chosen combination of input and output polarization, e.g. $p$-polarized incident light and $s$-polarized $2\omega$-light (abbreviated by $pS$). Standard boxcar-integrator technique was used for detection as described in detail in [20]. The SH signal has been normalized with respect to a reference that was generated in a quartz crystal in $pP$ configuration. The rotational anisotropy of the SH intensity was measured by rotating the sample around the surface normal (z-axis) as characterized by the azimuthal angle $\Psi$. The samples were oriented such that for $\Psi = 0^\circ$ ($180^\circ$) the [1 1 0]- ([1 1 0])-direction was lying within the plane of incidence (see figure 1(a)). The fluence of the incident laser radiation was kept at least one order of magnitude below 100 mJ cm$^{-2}$ which we determined as the threshold for multishot damage of our samples.

![Figure 1](image-url)

Figure 1. (a) Experimental setup. (b)–(f) Polar plots of the rotational SH anisotropy from five different GaP/Si(001) samples for different polarization combinations of the incoming fundamental and the detected SH as denoted in (b). For comparison, (g) and (h) show the signal of a GaP(001) wafer and a Si(001) wafer, respectively. The signals of the different polarization combinations have been scaled as denoted in the different figures for better comparison. Black lines in (a) exemplarily show fits of equation (1) for the polarization combinations $pP$ and $pS$.

The investigated GaP/Si heterostructures were grown by MOVPE in an Aixtron AIX 200 GFR reactor using triethylgallium (TEGa) and tertiary-butyl phosphine (TBP) as precursors for gallium and phosphorus, respectively. Four samples were prepared by using flow-rate modulated epitaxy (FME), for which TEGa and the TBP were supplied intermittently in a total of 16 cycles, starting with TEGa. The supply of GaP per cycle was varied between 0.2–1.36 monolayers by a
variation of the partial pressure of TEGa between $7.6 \times 10^{-4}$ and $7.6 \times 10^{-3}$ mbar while holding the TBP pressure constant at 0.91 mbar. In the following, these samples are referred to as FME0.20ML and so forth. For one sample, the continuous growth mode (CGM) was used, in which TEGa and TBP were applied simultaneously. The total thickness of the layers varied between 0.8 and 4.5 nm as determined by x-ray reflection in an X’Pert Pro diffractometer. The structural characterization of the GaP/Si interfaces was carried out in a JEOL 2200FS scanning transmission electron microscope operating at 200kV. This STEM can achieve atomic resolution in the high-angle annular dark-field imaging mode by aberration corrections of the probe forming lenses. For comparison, we also studied the SH response of the individual materials. In case of GaP, a 1 μm thick GaP film was grown epitaxially on a GaP(001) wafer.

The azimuthal dependence of the SH intensity for all samples and polarization combinations is presented in figures 1(b)–(h). These rotation patterns offer a direct access to the symmetry and rotational anisotropy of the second-order nonlinear response [3]. For the GaP wafer (figure 1(g)), a four-fold anisotropy was found for the polarization combinations $pP$, $pS$ and $sP$ in consistence with other reports [6]. This anisotropy results from the 43m-symmetry group of zinc-blende crystals and is a pure bulk dipole contribution. The $pS$ combination shows the strongest SHG; it vanishes completely for the SiO2 layer or the Si/SiO2 interface [5]. Within our detection limit, no SH signal could be observed in case of the $sS$ combination for both the GaP and the Si wafer.

Compared to the two individual wafers, the SH response of the five heteroepitaxially grown films of GaP on Si(001) (figures 1(b)–(f)) differs remarkably, both in overall intensity and in particular in anisotropy. Most prominent is the dominant isotropic contribution in the patterns for the $pP$ (blue lines) and the $sP$ (cyan lines) polarization combination. Except for the thinnest sample FME0.20ML, this signal is considerably larger than the response of the Si wafer. Moreover, it by far outreaches the almost invisible four-fold anisotropic bulk contribution of the GaP films on Si. We therefore assign the isotropic signal to the interface between GaP and Si. Since the GaP wafer was grown under similar conditions as the GaP/Si samples but does not show a measurable isotropic signal, we exclude that the GaP surface contributes significantly to the observed isotropic SH component. This interpretation is supported by additional measurements for GaP layers with thicknesses of up to 65 nm (not shown) which showed that the isotropic contribution of the SH response decreases exponentially with the GaP layer thickness.

A second-order nonlinear response of the interface between two semiconductors can arise either from the presence of a static electric field due to the band alignment of both materials [22] or from the modification of the chemical bonds at the interface. For the GaP/Si interface, the latter is related to the hybridized sp3 orbitals that are distorted due to the Ga–Si and P–Si bonds. Similar, although quantitatively stronger effects, have been observed for the clean Si surface, where a comparable symmetry break due to surface reconstruction results in an increase of the SH intensity by a factor of ~100 [23]. In our case of the GaP/Si interface, the increase compared to the oxidized Si surface is only a factor of ~10. This weaker effect might be connected to a cancelation due to bond distortions in opposite directions. An electric field at the interface gives rise to the EFISH-effect [24, 25], which also predominantly contributes to the p-polarized component of the SH intensity because it particularly affects the nonlinear response perpendicular to the interface. It has been demonstrated that fields due to depletion layers can exceed the nonlinear bulk response, even in case of strong bulk signals for III–V materials like GaAs [26, 27]. Most probably, both distorted bonds as well as electric fields at the interface contribute to the observed isotropic response.

The $pS$ contribution (red lines in figure 1) of the SH response seems to be less affected by the interface because its shape is similar to the response of the Si and the GaP wafer. Its strength, however, is almost five orders of magnitude smaller as compared to the bulk response of the GaP wafer. This is surprising because the penetration depth of the fundamental light

| Table 1. Isotropic and anisotropic contributions to the SHG from surface, bulk and EFISH of Si(001) and GaP(001) for the different polarization combinations. |
|---|---|---|---|---|
| Origin of SH | $pP$ | $pS$ | $sP$ | $sS$ |
| Si surface | $a_{pP}$ | $b_{pP}$ | $a_{pP}$ | — |
| Si surface | | | | |
| Si bulk (quadrupole) | $a_{pP}$ | $b_{pP}$ | $a_{pP}$ | — |
| Si EFISH | $a_{pP}$ | $b_{pP}$ | — | — |
| GaP bulk | $b_{pP}$ | $c_{pP}$ | $b_{pP}$ | — |
| GaP bulk (quadrupole) | $a_{pP}$ | $b_{pP}$ | $a_{pP}$ | — |
| GaP EFISH | $a_{pP}$ | $b_{pP}$ | — | — |

Figure 2. Isotropic and anisotropic coefficients for all investigated samples as obtained by a least-square fit of equation (1) for the polarization combinations $pP$, $pS$, and $sS$. 

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\( \delta_{\text{GaP}, 800 \text{nm}} \) is about 160 \( \mu \text{m} \) and the SH intensity increases up to a film thickness of \( \sim 30 \text{nm} \) before a reduction due to a phase shift between the \( \omega \) and \( 2\omega \)-light sets in. Therefore, the GaP bulk contribution from thin films of a few nm thickness should only be smaller by about one order of magnitude compared to the thick wafer. This strong reduction of the bulk response is most likely being caused by a destructive interference due to the appearance of anti-phase domains because the phase of the SH response originating from P-polar GaP is shifted by about \( \pi \) in comparison to the response of the Ga-polar GaP. This makes SHG very sensitive to APDs as it was demonstrated for thick GaAs films grown on Si(001) [28].

Beyond these general differences between the SH response of the individual wafers and the GaP/Si samples, the different heterostructures show characteristic variations for all measured polarization combinations. In the following we show that these individual differences of the SH response can be related to structural differences that have been obtained by STEM. This makes it possible to use the nonlinear response as a fingerprint of the GaP/Si interfaces.

For this purpose a symmetry analysis has been applied that quantifies the different isotropic and anisotropic contributions to the nonlinear response. Phenomenologically, the second-harmonic intensity \( I_y(2\omega) \) in reflection for a given polarization combination \( ij \) can be written as a function of the incidence intensity \( I_i(\omega) \) as

\[
I_y(2\omega) \propto |x_{\text{eff},ij}^{(2)}|^2 I_i(\omega)
\]

where \( x_{\text{eff},ij}^{(2)} \) is an effective second-order nonlinear susceptibility tensor of third rank that includes all contributions (surface, interface, bulk, EFISH, etc) to the second-order nonlinear polarization [3] even if the intrinsic material response of the bulk and EFISH contributions might be in the most general case described by higher-order tensors of the nonlinear susceptibility \([25, 29]\).

The dependence of \( I_y(2\omega) \) on the azimuthal angle \( \Psi \) can then be written as a Fourier expansion up to the fourth order

\[
I_y(2\omega) \propto |a_{ij} + \sum_{m=1}^{4} b_{ij}^{(m)} \cos m\Psi + c_{ij}^{(m)} \sin m\Psi|^2,
\]

where the isotropic \((a_{ij})\) and anisotropic coefficients \((b_{ij}^{(m)}, c_{ij}^{(m)})\) contain all optical properties, in particular the corresponding components of the nonlinear susceptibility tensors as well as Fresnel coefficients. For (001) oriented samples, odd orders \( m \) can be excluded.

Table 1 lists the expected non-vanishing isotropic and anisotropic coefficients at the different polarization combinations for all considered SHG sources, i.e., Si-surface, -bulk and -EFISH as well as GaP-bulk and -EFISH.

Within this model the azimuthal dependence of the SH intensity can be well described for all polarization combinations by a least-square fit of the coefficients \( a_{ij}, c_{ij}^{(2)}, c_{ij}^{(4)} \) and \( b_{ij}^{(2)}, b_{ij}^{(4)} \), i.e., omitting the \( c_{ij}^{(4)} \). Two examples of these fits for the polarization combinations \( pP \) and \( pS \) are shown in figure 1(b) (black lines).

Figure 2 summarizes the fitting results for the polarization combinations \( pP, pS, \) and \( sS \). For all heterostructures, the interface specific isotropic parameter \( a_{ij} \) (blue bars) dominates the total response. For the sample with the smallest GaP thickness of 0.8 nm (FME0.20ML), the magnitude of this contribution is comparable to that of the Si wafer. For the other GaP/Si samples including the CGM sample, \( a_{ij} \) shows only a small variation. This suggests that the interface properties do not change substantially for GaP layer thicknesses of 1.6–4.5 nm.

The STEM images show, however, that the number of defects in the interface-near region of the FME samples increases considerably for a GaP supply of more than 1 ML per cycle. This is shown exemplary in figures 3(a) and (c) by comparing the STEM images of FME0.97ML and FME1.30ML. Whereas the GaP film of sample FME0.97ML
shows no visible defects and a rather abrupt interface, two APDs of opposite polarity can be identified in the left and right part of the STEM image of sample FME1.30ML. These APDs can form if an excess of TEGa etches Ga droplets into the Si crystal which then serve as nuclei for APDs [30]. The formation of APDs causes an in-plane symmetry reduction that affects predominantly the in-plane (s-polarized) SHG components. This is directly reflected by the strong increase of the isotropic $a_{SS}$ contribution (yellow bars in figure 2) as observed for the CGM sample. In contrast, $b_{pp}^{(2)}$ and $b_{ps}^{(4)}$ which are depicted by orange and red/white bars in figure 2, respectively. These parameters might be further indicators for the film quality. They show, however, no clear trend for the different growth modes and cannot be correlated to specific defects observed in STEM.

In summary, we have shown that optical second-harmonic generation can be successfully used as a sensitive, non-invasive probe for the quality of the interface between thin films of GaP and Si(001). The rotational anisotropy of the second-harmonic intensity can be correlated to specific defects that form at different growth conditions in metal–organic vapor phase epitaxy. In particular, the occurrence of anti-phase domains and twins are clearly identified. This all-optical technique can be applied as an in situ monitor of the growth process complementary to reflection anisotropy spectroscopy.

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