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Interface-Specific Excitation of Coherent Phonons at the Buried GaP/Si(001) Heterointerface

Gerson Mette, Kunie Ishioka, Steven Youngkin, Wolfgang Stolz, Kerstin Volz, and Ulrich Höfer**

Ultrafast charge-carrier and phonon dynamics at the buried heterointerface of GaP/Si(001) are investigated by means of two-color pump-probe reflectivity measurements. The carrier-induced reflectivity signal exhibits a resonant enhancement at a pump-photon energy of 1.4 eV, which is assigned to an optical transition at the interface. In addition, the transient reflectivity is modulated by a coherent oscillation at 2 THz, whose amplitude also becomes maximum at 1.4 eV. The observed resonant behavior of the oscillation, in combination with the characteristic wavelength-dependencies of its frequency and its initial phase, strongly indicates that the 2-THz mode is a difference-combination mode between a GaP-like and a Si-like phonon at the heterointerface and that the corresponding second-order Raman scattering process can be enhanced by a double resonance involving the interfacial electronic states.

1. Introduction

The coupling of charge and lattice degrees of freedom in semiconductors is one of the key factors to determine their crystalline structure and dominate the electronic, optical and thermal properties.[1] At surfaces of inorganic semiconductors, the rearrangement of the atomic structure leads to well-defined electronic and phononic surface states.[2] Although similar effects are expected at deeply buried semiconductor interfaces, those are more challenging to investigate due to the experimental difficulty in detecting and isolating weak interface signatures from dominant bulk signals. Highly interface sensitive nonlinear optical techniques such as second-harmonic generation (SHG) spectroscopy have been applied to study electronic interface states.[3] Phonons, however, are even more difficult to investigate by SHG due to their tiny modulating signals in the time domain.[4,5] In this study, we therefore choose an alternative approach to explore the ultrafast charge-carrier and phonon dynamics at a buried GaP/Si(001) heterointerface: Instead of an interface-sensitive detection, we apply an interface-specific excitation and then detect the small signal modulations due to the interface phonons with a linear optical technique.

GaP/Si(001) has recently gained attention as an interesting model interface between a polar and a non-polar material.[6–12] Since the two semiconductors have only a small mismatch in their lattice constants, the interface can serve as a template for Si-based III/V optoelectronics.[6–8] The atomic structure and morphology of the interface is well characterized.[6,7,10–12] For a wide range of growth conditions, the interface mainly consists of charge-neutral (112) and (111) pyramidal facets extending over seven lattice planes.[11] A recent SHG study revealed an optical resonance of the interface at 1.4 eV.[13] This resonance has been attributed to interface electronic states which lie energetically in the optical band gap of the two semiconductors.[13–15] Previous transient reflectivity measurements at GaP/Si(001) heterostructures with above-bandgap photoexcitation of GaP and Si at 3.1-eV photon energy[16–18] revealed the generation of coherent longitudinal optical and acoustic phonons of the respective bulk semiconductors.[16,18] The main effect of the interface was the generation and observation of acoustic strain pulses,[17,18] however, no phonon mode characteristic to the heterointerface was observed.

In the present study, we make use of short-pulsed, tunable near-infrared pump light in order to resonantly excite the interface for the investigation of the interfacial charge-carrier and phonon dynamics with transient reflectivity measurements. The measured carrier-induced reflectivity response exhibits a clear resonance at 1.4 eV in agreement with the previous SHG results.[13] Moreover, the transient reflectivity signals are modulated by an oscillation at 2 THz, whose amplitude follows the

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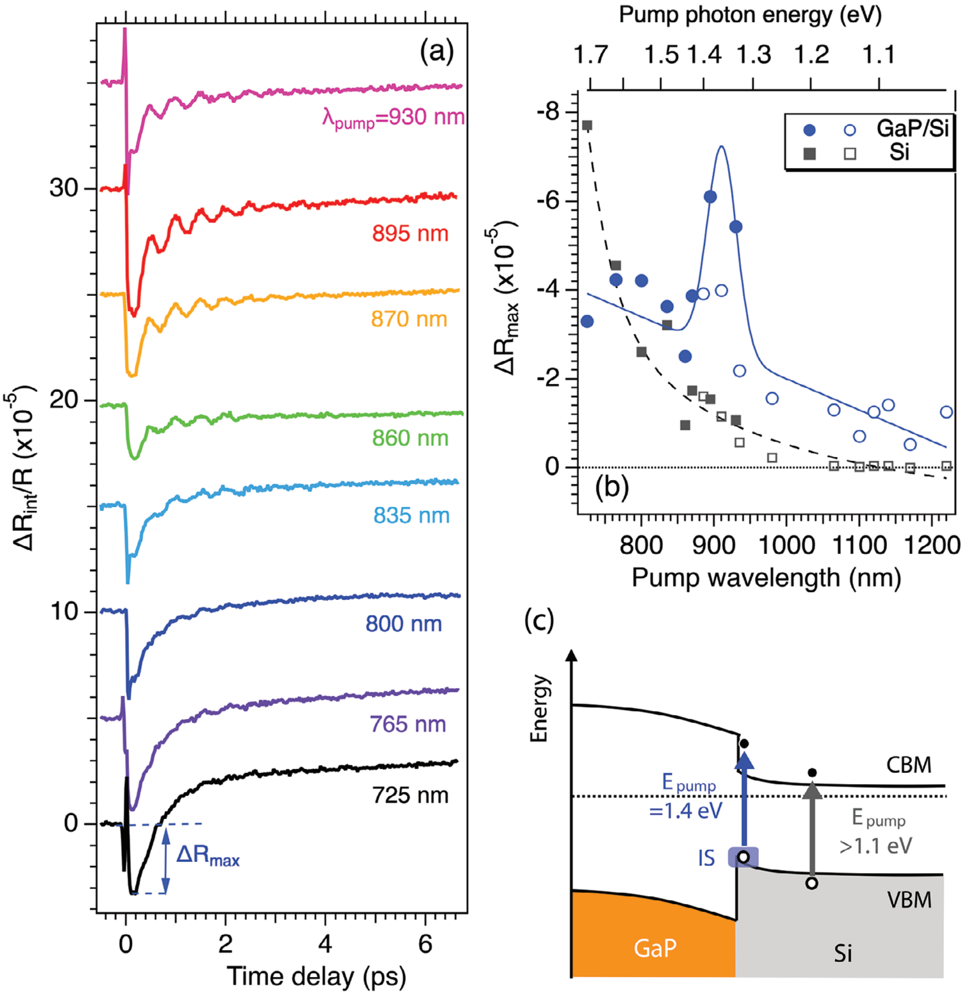

Figure 1. a) Interface-contribution in transient reflectivity of the GaP/Si heterostructure pumped at different wavelengths and probed at 800 nm. Traces are offset for clarity. b) Height of the initial drop ΔR_{max} of the interface contribution of GaP/Si as a function of the pump wavelength in comparison to bulk Si. Filled and open symbols are obtained with two different light sources. The latter are multiplied by 1.7 to scale to the former. Curves are to guide the eye. c) Schematic band diagram of the GaP/Si interface with IS indicating an occupied interface state.[13]

same resonance as the carrier-induced response and which is absent in the reflectivity signals of the bulk semiconductors. The consistent resonant behavior unambiguously proves that this oscillation is an interface phonon mode. The observed wavelength-dependencies of, both, frequency and initial phase of the 2-THz mode furthermore suggest that the interfacial phonon is enhanced by a double resonance involving the interface electronic states.

2. Results and Discussion

The as-measured transient reflectivity signals ΔR from the GaP/Si sample (cf. Figure S2a, Supporting Information) contain contributions not only from the GaP overlayer/heterointerface ΔR_{int} but also from the Si substrate ΔR_{sub}.[19] Therefore, we extract the former contribution by subtracting the latter from the as-measured signal ($\Delta R_{\mathrm{int}} \equiv \Delta R - \Delta R_{\mathrm{sub}}$) as described in more detail in Section III (Supporting Information). Please note, that a coherent upgoing spike at $t = 0$ originating from a contribution of the Si substrate[20] was not completely eliminated by the subtraction for some of the transients. Pump-induced reflectivity changes in general can be associated with changes in the dielectric function due to the presence of free charge carriers (electron–hole plasma) as well as interband transitions (state-filling effect).[20] For Si bulk samples and low excitation densities, one would expect a pump-induced decrease of the reflectivity from both contributions in accordance with our results obtained on Si without a GaP overlayer (Figure S2b, Supporting Information) and previous studies.[20–22]

Figure 1a compares the obtained overlayer/interface-contribution $\Delta R_{\mathrm{int}}/R$ for different pump wavelengths. The transients show an abrupt drop at $t = 0$ which is followed by a double exponential increase. The height of the initial drop ΔR_{max} gives a semi-quantitative measure for the photoexcited charge-carrier density in the overlayer and at the heterointerface. ΔR_{max} exhibits a distinct resonance peak at $\lambda_{\mathrm{pump}} \simeq 900$ nm (photon energy of 1.4 eV) on top of the monotonic decrease with increasing wavelength (decreasing pump-photon energy) as plotted in Figure 1b. This resonance behavior coincides with

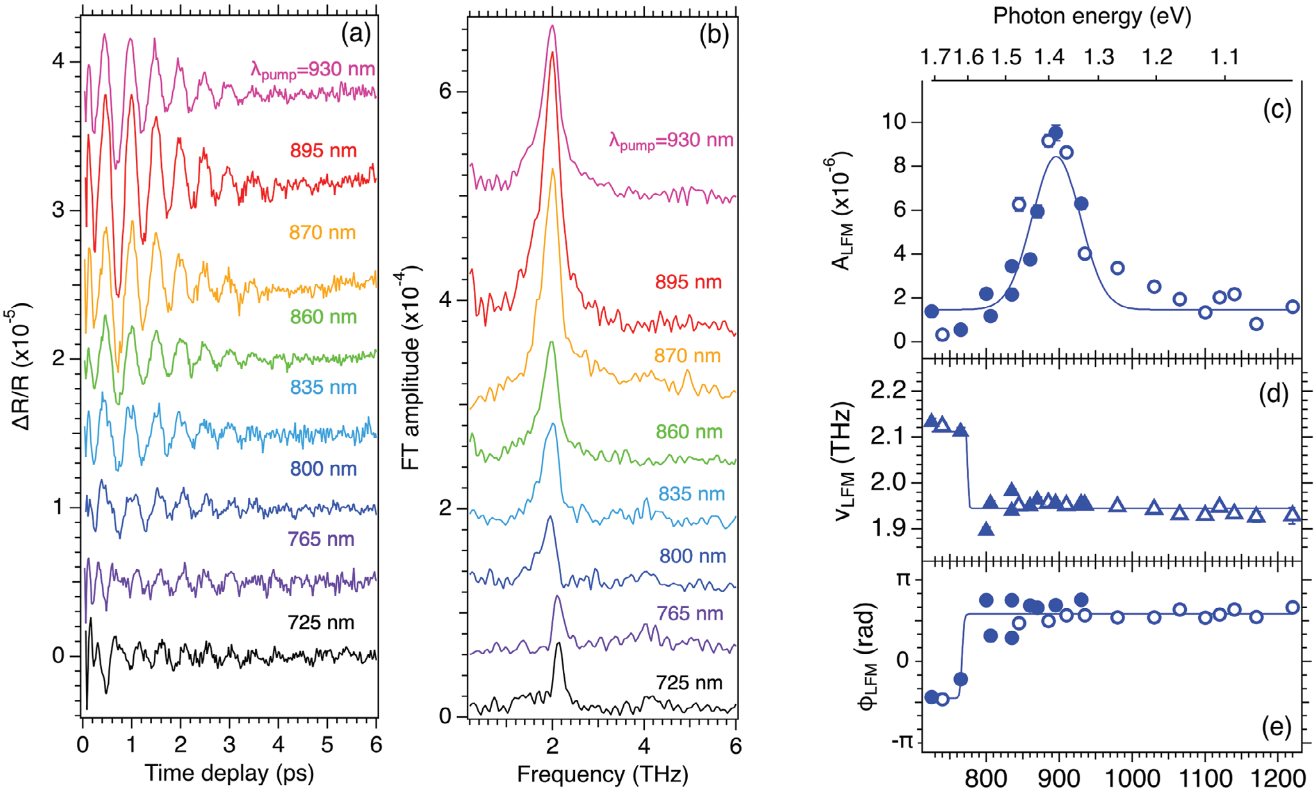

Figure 2. a) Oscillatory part of transient reflectivity of GaP/Si pumped at different wavelengths and b) the corresponding fast Fourier transform (FFT) spectra. Traces are offset for clarity. c) Amplitude, d) frequency, and e) initial phase of the low-frequency mode (LFM) as a function of the pump wavelength. Filled and open symbols in each panel represent the results obtained with two different light sources. In (c) the latter are multiplied by 1.7 to scale to the former. Curves are to guide the eye.

the resonance of the fast SHG component obtained in our previous study on a thin ($d = 4.5$ nm) GaP film on Si(001).[13] Indeed, it is in apparent contrast to the initial drop height of bulk Si (transient signals shown in Figure S2b, Supporting Information), which decreases monotonically with decreasing photon energy, as plotted in the same figure. We therefore attribute the 1.4-eV resonance to an optical transition at the interface[13] as schematically shown in Figure 1c. After the initial drop of the reflectivity induced e.g. by a state-filling effect of the involved electronic states, the following increase of $\Delta R_{\text{int}}/R$ can be fitted to a multiple exponential function. The time constant for the fast rise of ≈0.2 ps is comparable to the fast decay of the SHG signal observed previously[13] and it is assigned to the relaxation of the excited electronic states. The slower rise occurs on a similar time scale to that of bulk Si (cf. Figure S2b, Supporting Information), ≈40 ps, and is therefore attributed to carriers photoexcited in the Si substrate and recombining at the GaP/Si interface.[19,20,23]

The transient reflectivity signals of the GaP/Si sample also exhibit an apparent periodic modulation, as extracted in **Figure** 2a after subtracting a multi-exponential baseline. This oscillation is not seen for bulk Si (Figure S2b, Supporting Information) or bulk GaP (not shown) measured under the same conditions. Indeed, the frequency of this oscillation, 2 THz, has no counterpart in the previously reported first- and second-order Raman spectra of bulk GaP or Si.[24,25] Hereafter we refer to the 2-THz oscillation as "low-frequency mode (LFM)." In the fast Fourier-transform (FFT) spectra in Figure 2b, we also see a small overtone of the LFM at ≈4 THz for λ_{pump} <800 nm.

The oscillatory reflectivity in Figure 2a can be fitted reasonably to a damped harmonic oscillation:

$$f(t) = A_{\text{LFM}} \exp(-\Gamma_{\text{LFM}} t) \sin(2\pi \nu_{\text{LFM}} t + \phi_{\text{LFM}}) \tag{1}$$

The obtained fitting parameters A_{LFM}, Γ_{LFM}, ν_{LFM} and ϕ_{LFM} are plotted as a function of λ_{pump} in Figure 2c–e. The amplitude A_{LFM} in Figure 2c exhibits a distinct resonant peak at λ_{pump} ≃900 nm (photon energy of 1.4 eV). This resonance behavior coincides with that of ΔR_{max} in Figure 1b, indicating a strong coupling of the LFM with the interface electronic state. We therefore assign the LFM as an interface phonon mode coupled with the electronic transition at the GaP/Si interface. We note that the frequency ν_{LFM} (Figure 2d) exhibits a small but distinct jump, whereas the initial phase ϕ_{LFM} (Figure 2e) shows a shift by π, both at λ_{pump} ~800 nm, which corresponds to our probe wavelength.

As for the microscopic origin of the 2-THz interface phonon mode, it might be natural to consider Ga-Si or P-Si bonds at the heterointerface, where the electronic interface states are expected to be localized.[14] Stretching vibrations of these "wrong" bonds would appear at frequencies comparable to those of the optical phonons of bulk GaP and Si, however, which are in the

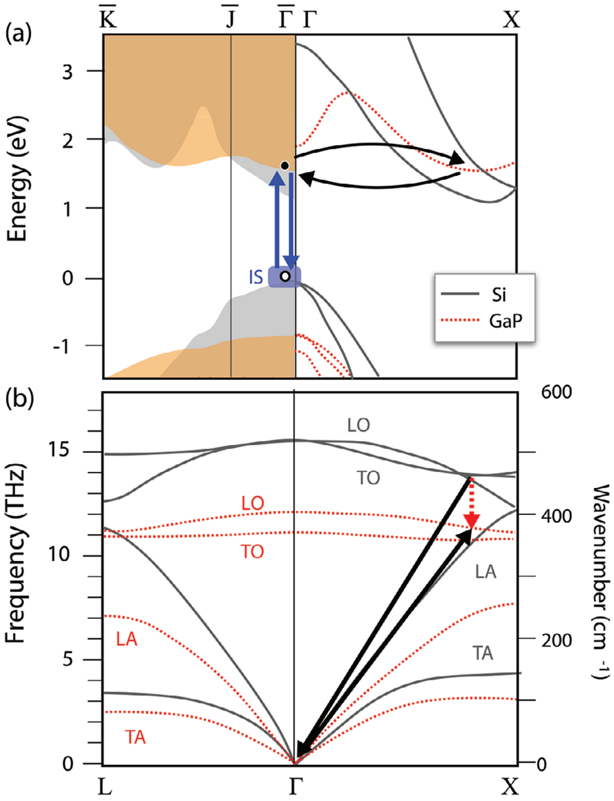

Figure 3. a) Schematic illustration of doubly resonant second-order Raman scattering at the GaP/Si interface (arrows). Left: Calculated projected band structures of GaP(001)[35] (shaded in orange) and Si(001)[36] (grey) superposed with a valence band offset of 0.8 eV. The conduction bands were both shifted to represent the actual band gaps of Si (1.12 eV) and GaP (2.24 eV). IS indicates an occupied interface state near the Γ-point.[13] Right: Calculated bulk band structure of GaP[37] (red dotted curves) and Si[27] (grey solid curves) superposed with the same valence band offset of 0.8 eV. b) Phonon dispersion curves of Si and GaP taken from refs. [38,39] with an example of a pair of Si and GaP optical phonons participating in the second-order scattering (black arrows).

much higher frequency range of 12–15 THz.[26,27] It is highly unlikely that the chemical bonds at the interface can be weakened so much as compared to the bulk that their frequency lowers by a factor of five or more. Instead, one could consider a combination mode among the interface vibrational modes. Previous Raman studies on GaAs/AlAs superlattices reported higher-order scattering by multiple phonons in addition to the first-order scattering by a single phonon.[28–34] The intensities of the higher-order Raman scattering are usually much smaller than those of the first-order, but the former can be enhanced significantly by tuning the incident photon energy to the transition between the sub-bands of a quantum well, for example. Multiple scattering can involve not only phonons within the same crystal, but also those from two different materials, e.g. GaAs and AlAs. Whereas most of these studies focused on sum-frequency combination modes appearing at high frequencies, there was also a report on a Raman peak appearing at a low frequency of 108 cm^{-1} (3.2 THz).[33] Based on its resonance behavior it was attributed to a difference-frequency combination mode involving GaAs and AlAs optical phonons.

In the present study we similarly attribute the observed LFM to a difference-frequency combination mode between a GaP-like and a Si-like optical phonon. Because the optical phonon branches of GaP and Si have comparatively small dispersion along the $\Gamma - X$ direction of the Brillouin zone as shown in **Figure 3b**, there is a relatively high density-of-states for a pair of Si and GaP optical phonons to simultaneously satisfy energy and momentum conservation, i.e., $\nu_{\mathrm{Si}} - \nu_{\mathrm{GaP}} = 2$ THz and $\boldsymbol{k}_{\mathrm{Si}} = -\boldsymbol{k}_{\mathrm{GaP}}$. An exemplary second-order Raman scattering process that would give rise to such a difference-frequency combination mode is shown schematically in Figure 3a. It is initiated by the creation of electron-hole pairs upon optical excitation at the Γ-point, followed by the large-$\boldsymbol{k}$ scattering of a Si-like and a GaP-like optical phonon and finally terminated by the charge-carrier recombination.

As a combination phonon mode, the coherent LFM is detected with an extraordinarily large amplitude. We attribute the significant enhancement to a double (or multiple) resonance involved in the second-order Raman scattering. Figure 3a illustrates an example of such a doubly resonant second-order scattering, in which the excited state at the Γ-point and the GaP conduction band near the X-point contribute as real intermediate states. Here, the excited state at the Γ-point originates from GaP conduction band states projected to the (001) interface as schematically shown in the left part of Figure 3a. Alternatively, one could also consider the existence of unoccupied electronic interface states as DFT band structure calculations have predicted the existence of both occupied and unoccupied electronic interface states at the GaP/Si interface.[14] The involvement of a double resonance can also explain the small discontinuity in the LFM frequency at $\lambda_{\mathrm{pump}} \simeq \lambda_{\mathrm{probe}}$ shown in Figure 2d. The π-phase shift observed in Figure 2e is an indication of Stokes and anti-Stokes scattering dominating the detection process in the short ($\lambda_{\mathrm{probe}} < \lambda_{\mathrm{pump}}$) and long ($\lambda_{\mathrm{probe}} > \lambda_{\mathrm{pump}}$) probe wavelength regimes, respectively.[40] A small frequency disparity between Stokes and anti-Stokes scattering can be explained as a result of different intermediate electronic states contributing to the double (or multiple) resonance, as reported for the disorder-induced Raman bands (D, D', D'' and their combination modes) of graphitic materials.[41–45]

3. Conclusion

In conclusion, our two-color transient reflectivity measurements applied an interface-specific excitation to explore the ultrafast charge-carrier and phonon dynamics at the buried heterointerface of GaP/Si(001). By using tunable near-infrared pump light, an interface phonon mode was unambiguously resolved as a periodic modulation at ≈2 THz, whose amplitude was resonantly enhanced by an optical transition involving electronic interface states. The oscillation was interpreted as a difference-frequency combination mode between a GaP-like and a Si-like optical phonon. Its unusually large amplitude, together with its photon-energy dependent frequency, indicated the involvement of a multiple resonance in the second-order Raman scattering. We thus demonstrated electron-phonon coupling that is characteristic to a heterointerface of polar and non-polar inorganic semiconductors.

4. Experimental Section

The studied sample was a nominally undoped 10-nm thick GaP nucleation layer grown at 450°C on *n*-type Si(001) by using flow-rate modulated metal-organic vapor phase epitaxy (MOVPE).[46,47] The single crystalline GaP nucleation layer exhibited a small surface undulation with a lateral feature size of ≤30 nm as shown in Figure S1 (Supporting Information). Two-color pump-probe reflectivity measurements were performed under ambient conditions in the near back-reflection geometry. Details of the experimental setups are described in Section II (Supporting Information). Two different sets of tunable femtosecond light sources with pulse durations in the range of 30 − 50 fs were employed to cover the pump wavelength range of 720 − 1220 nm (photon energy of 1.02 − 1.72 eV). Please note, that the used pulse durations were not short enough to observe the optical phonons of bulk GaP and Si (frequencies 12 and 15.6 THz, respectively).[26,27] The pump-photon energies were smaller than the indirect bandgap of GaP (2.26 eV), but comparable with or larger than that of Si (1.12 eV). The probe wavelength was fixed at 800 nm (1.55 eV). The pump-induced change in the reflectivity $\Delta R/R$ was measured by detecting the probe lights before and after the reflection by the sample with a pair of matched photodiodes. The time delay t between the pump and probe pulses was scanned using a linear motor stage with a slow scan technique.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

buried heterointerface, coherent phonons, experiment, GaP/Si(001), interface phonon, pump-probe, transient reflectivity, ultrafast dynamics

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