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Shift currents from symmetry reduction and Coulomb effects in (110)-orientated $GaAs/Al_{0.3}Ga_{0.7}As$ quantum wells

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We report on the observation of an additional shift current tensor element by interband excitation of undoped (110)-oriented $GaAs/Al_{0.3}Ga_{0.7}As$ quantum wells with a 150 fs laser pulse. The additional tensor element results from the symmetry reduction of the quantum well structure and shows a strong enhancement and a phase shift at the light-hole exciton transition revealing that shift currents are a sensitive probe of Coulomb effects in semiconductors. Moreover, we show that the overall shift current does not directly follow the envelope of the optical excitation pulse but contains a noninstantaneous contribution.

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Using nonlinear $\chi^{(2)}$ effects in semiconductors it is possible to generate electrical currents by purely optical excitation. In general, the complex quantity $\chi^{(2)}$ which is responsible for the current generation can be divided into three terms: the rectification current, the shift current, and the injection current.[1] Each of these three components contributes to the overall current response and has recently attracted a lot of attention.[2–6] The rectification current results from a polarization of virtual carriers and exists for all photon energies of the optical excitation pulse. In contrast, shift and injection currents involve real carriers and, thus, rely on the use of resonant excitation schemes. The injection current results from a quantum interference process, whereas the shift current arises from a spatial shift of the electron charge during excitation.

Shift currents are sometimes also referred to as linear photogalvanic (or photovoltaic) currents[4] or "above-band-gap optical rectification."[2,7] The first experimental[8,9] and theoretical[10] investigations on shift currents used ferroelectric crystals but it was soon recognized that shift currents may also occur in noncentrosymmetric crystals with no polar axis.[11] Lately, shift currents have again been the subject of intense investigation, mainly because they allow for the generation of free-space THz radiation.[1–3,5,7,12] So far, shift currents generated by interband excitation have only been studied experimentally in bulk semiconductors. The shift current tensor elements that can arise from the symmetry reduction in quantum well (QW) structures have only been treated theoretically.[13] Moreover, all previous theoretical and experimental investigations of shift currents have been interpreted by invoking only free carriers effects. The influence of Coulomb effects on shift current generation has neither been studied experimentally nor theoretically.

In this Rapid Communication we report on the investigation of symmetry reduction and Coulomb enhancement effects on shift current generation in (110)-oriented GaAs/AlGaAs quantum wells. We observe an additional shift current tensor element which only exists in the QW structure and not in the corresponding bulk material. Spectrally resolved measurements of this shift current element allow one to make an experimental distinction between heavy- and light-hole shift currents. The amplitude spectrum of the shift current component exhibits surprising features, among them a strong enhancement of the current at the light-hole exciton resonance.

The shift current experiments were performed on two different QW samples. The samples consist of 40 periods of $GaAs/Al_{0.3}Ga_{0.7}As$ QWs and a 500 nm thick buffer layer grown on a 500 μm thick, (110)-oriented GaAs substrate. In both samples the wells and the barriers are 8 nm thick. Sample No. 1 is undoped, whereas the barriers of sample No. 2 are n-doped with a Si concentration of 8×10^{10} cm^{-2} (delta doping in the middle of the barriers). A 150 fs, 76 MHz Ti:sapphire oscillator was used to excite the samples at normal incidence with a peak intensity of the optical pulses of 60 MW/cm^2 resulting in a typical average carrier density of 2×10^{11} cm^{-2}. The shift currents were detected with a standard free-space THz setup which is described elsewhere.[14] This THz setup allows us to detect currents flowing in a certain direction in the plane of the QWs. All experiments were done at room temperature.

We first comment on the sample properties. In the following discussion we take the x, y, and z directions to be parallel to the crystal's $[001]$, $[1\bar{1}0]$, and $[110]$ directions, respectively. The corresponding sample orientation is shown in the inset of Fig. 1. In the (110)-oriented GaAs QWs the well-barrier interfaces reduce the point group symmetry to C_{2v} as compared to bulk GaAs with a T_d point group. In the QW structure the shift current tensor has seven nonzero components: *xxx*, *xyy*, *xzz*, *yxy*, *yyx*, *zxz*, and *zzx*.[14,15] Of these tensor elements only the *xxx* element results from the symmetry reduction. All other elements also exist in (110)-oriented bulk material with a T_d point group, even though their value does not have to be the same as in the T_d structure. Using the *xxx* tensor element for the generation of shift currents ensures that the current signal originates exclusively from the QW region and is not superimposed on signals from the bulk continuum. This is a specific advantage of an *xxx* shift current study since it allows for an investigation of symmetry properties and other effects in quantum confined structures.

We have also used cw photoluminescence excitation (PLE) spectroscopy to optically characterize the QW samples. In these measurements the photoluminescence

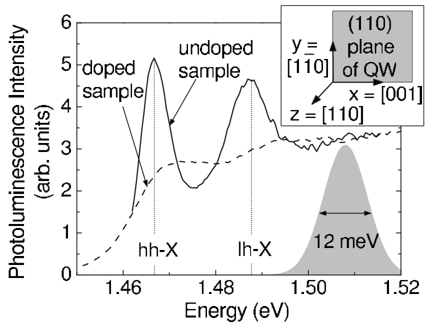

FIG. 1. Photoluminescence excitation (PLE) spectrum of the undoped (solid line) and doped (dashed line) QW sample measured with a cw laser at room temperature. The arrows mark the $n=1$ hh-X and lh-X transitions. The gray area shows the spectral width of the pump pulse used in the THz experiments.

emitted from the samples was measured versus excitation photon energy of a cw laser source. The PLE spectra to an extent reflect the absorption spectra of the sample. In Fig. 1 are shown the PLE spectra from the doped and undoped QW samples. The spectrum of the doped sample has been normalized so that the photoluminescence intensity at 1.51 eV is the same as in the spectrum of the undoped sample. In the PLE spectrum of the undoped sample one clearly sees the $n=1$ heavy-hole exciton (hh-X) and the $n=1$ light-hole exciton (lh-X) resonances.[16] However, no distinct peaks can be observed in the PLE curve of the n-doped sample. This is due to screening of the Coulomb attraction by free carriers, which, in turn, weakens the exciton binding energy and decreases the strengths of the exciton resonances. Also shown in Fig. 1 as a gray background is the 12 meV broad spectrum of the femtosecond laser used as the excitation source in the THz experiments. The center photon energy of this laser pulse can be spectrally tuned to enable different excitation conditions.

We now describe the shift current experiments. In all the measurements the THz polarizer was adjusted to transmit the THz radiation resulting from currents flowing in the $x=[001]$ direction and the polarization of the pump pulses was either parallel to the $x=[001]$ or $y=[1\bar{1}0]$ directions. This geometry allowed for the detection of *xxx* and *xyy* shift currents, respectively. The measured THz traces were treated as follows. The measurements were taken in pairs with the sample being rotated by 180° in between each individual measurement. The rotation reversed the shift current flow and, consequently, the measured THz trace was inverted. The two recorded time traces were then subtracted from each other so that the resultant time trace corresponds to twice the THz shift current signal. This technique ensured that any polarization independent background signal was eliminated.

In Fig. 2(a) are plotted the THz signals emitted from the undoped sample when it was excited with light linearly polarized along the y direction (*xyy* tensor element, dashed line) and the x direction (*xxx* element, solid line). We used an excitation photon energy of 1.518 eV, which led to the excitation of both free electron-heavy-hole pairs and free electron-light-hole pairs with relatively small excess energy, see Fig. 1. A distinct THz trace arising from the *xyy* tensor element was observed, yet, within our experimental uncer-

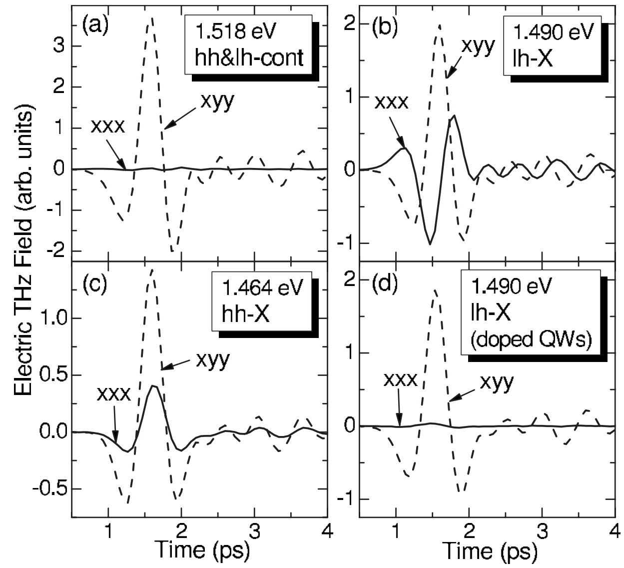

FIG. 2. (a)–(c) THz traces resulting from xyy shift currents (dashed lines) and *xxx* shift currents (solid lines) in the undoped QW sample for different excitation photon energies. (d) THz traces emitted from the doped sample for an excitation energy corresponding to the lh-X energy.

tainty no *xxx* signal could be observed. This is in line with previous observations.[14] When the excitation photon energy was reduced to be coincident with the lh-X resonance [Fig. 2(b)], a clear *xxx* THz signal was observed, with a peak-to-peak amplitude that is approximately 60% of the amplitude of the *xyy* signal. If we further reduced the excitation photon energy to the hh-X resonance [Fig. 2(c)], the *xxx* signal persisted, although with a reduction in the peak-to-peak amplitude. An additional interesting feature seen in Fig. 2 is that the shape of the *xxx* THz trace and, thus, also the phase of the *xxx* shift currents depend on the excitation photon energy. We also tried to measure *xxx* shift currents in the doped QW sample. No *xxx* shift current signals could be measured for the photon energies as described above, this is illustrated in Fig. 2(d) for an excitation photon energy equal to lh-X resonance of the undoped sample. It should be emphasized that except for the doping the two samples are identical. The suppression of the shift current in the doped sample demonstrates that the Coulomb interaction and, in particular, the existence of exciton absorption substantially affects shift current generation.

To investigate the spectral dependence of the *xxx* shift current in more detail, we first concentrate on the amplitude of the signal.[17] In Fig. 3(a) the peak-to-peak amplitude of the *xxx* THz signal emitted from the undoped QW sample is plotted as filled squares versus excitation photon energy. This graph not only confirms the results shown in Fig. 2 but also reveals new aspects of the interactions. The maximum THz amplitude occurs exactly at the photon energy of the lh-X resonance. If the photon energy was increased above the lh-X resonance initially the signal vanished and only at photon energies >1.54 eV could a *xxx* shift current signal be again reproducibly measured. Thus we conclude that excitation of continuum states with a relatively large excess energy also allows for the generation of *xxx* shift currents.[18] Results of

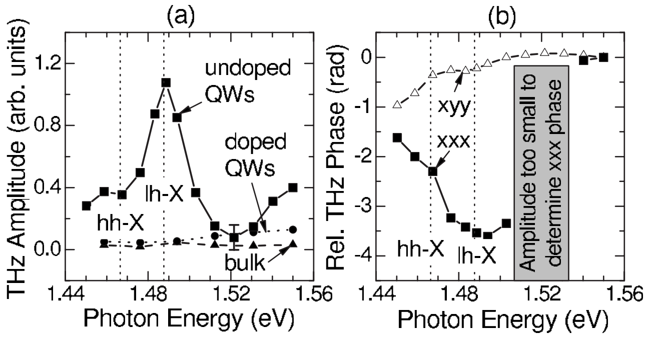

FIG. 3. (a) Amplitude of the THz traces of *xxx* shift currents versus excitation photon energy. Filled squares: undoped QW sample, filled circles: doped QW sample, and filled triangles: bulk sample. (b) Phase of the $f=1.4$ THz frequency component of the THz traces resulting from the *xxx* shift current (filled squares) and the xyy shift current (empty triangles) versus excitation photon energy.

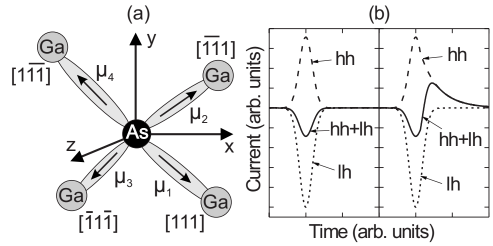

FIG. 4. (a) Illustration of the four bonding orbitals in the GaAs lattice. Each As atom is surrounded by four Ga atoms with the four bonds being oriented along the $\langle 111 \rangle$ directions. Resonant excitation of this structure may lead to changes of the dipole moments, μ_i, pointing along the bond directions. (b) Superposition of heavy-hole (hh) and light-hole (lh) currents with identical (left-hand side part) and with different (right-hand side part) temporal shapes.

the same experiment are plotted for the doped QW sample and for a (110)-oriented bulk GaAs sample, which is identical to the substrate on which the QWs have been grown. No clear *xxx* shift current signal is detected in either case. The absence of *xxx* shift currents in bulk GaAs provides evidence that it is the QW region which is responsible for the creation of the *xxx* shift current signal, while the absence of *xxx* shift currents in the doped QW sample provides further evidence that the Coulomb interaction enhances the shift current signal.

Before proceeding with a more detailed discussion of the spectral dependence of the amplitude of the *xxx* shift current we will address the spectral dependence of its phase. In Fig. 3(b) the phase of the spectral maximum of the *xxx* THz traces emitted from the undoped sample are plotted as filled squares (the spectral maximum occurs at 1.4 THz, see also Ref. 19 in which a similar analysis has been done for the injection currents). The phase at the largest photon energy has been set to zero. In this spectral range we expect that the shift current would be dominated by electron-heavy-hole excitation due to the larger oscillator strength of electron-heavy-hole transitions compared to electron-light-hole transitions.[20] The gray background marks the spectral range in which the amplitude of the *xxx* THz trace was too small to determine the phase. If the excitation photon energy was decreased further to be coincident with the energy of the lh-*X* the phase changed by a value of approximately π compared to the phase obtained by excitation in the continuum. This phase change corresponds to a current reversal. At the lh-*X* energy the excitation of electron-light-hole pairs is maximized, see Fig. 1. Consequently, we attribute the current reversal to a physical phenomenon which is different for excitation of electrons from heavy- and light-hole confined states. To explain this behavior we use the model proposed by Khurgin.[13] The ionic bonds of a GaAs lattice result in permanent dipole moments along the different diagonal axes, i.e., along the four $\langle 111 \rangle$ axes. In equilibrium the four dipole moments cancel so that the net dipole moment is zero. Charge transfer, which can only occur along the $\langle 111 \rangle$ axes, leads to changes of the permanent dipole moments expressed by $\Delta\mu_i$, $i=1,\ldots,4$ [see Fig. 4(a)]. It can be shown that excitation of free-electron-heavy-hole pairs in (110)-oriented GaAs QWs[21] leads to a dipole moment along the $[00\bar{1}]$ axis since $\Delta\mu_1$, $\Delta\mu_2 < \Delta\mu_3$, $\Delta\mu_4$. In contrast, excitation of free-electron-light-hole pairs leads to dipole moment along the [001] axis since $\Delta\mu_1$, $\Delta\mu_2 > \Delta\mu_3$, $\Delta\mu_4$. It is these oppositely oriented dipole moments that are responsible for the current reversal. It should be noted that the calculation of Ref. 13 was performed for free-electron-hole transitions. We have no reason to assume that a similar picture does not hold for excitonic excitation since the symmetry of the GaAs lattice is not changed by the Coulomb attraction.

The phase dependence shown in Fig. 3(b) allows us to draw another important conclusion with regard to the shift current dynamics. If the excitation photon energy is tuned from the lh-*X* to smaller energies, the phase increases. This is as expected since heavy-hole transitions become dominant which leads to a reversal of the current flow. Surprisingly, however, we do not observe a phase jump of π but a gradual phase change of less than π. Additionally, the current amplitude does not go to zero when the photon energy is decreased and heavy-hole transitions become dominant. We believe that this behavior is evidence that the exciton-driven shift current does not directly follow the optical pulse envelope. This is substantiated by a very simple model. In the left-hand side part of Fig. 4(b) two oppositely oriented current pulses with identical temporal shapes (named hh current and lh current) are shown. A superposition of these two current pulses will result in a current pulse with the same temporal shape (named hh+lh current). This shape does not depend on the ratio of the two current amplitudes. Therefore an arbitrary frequency component of the lh+hh current pulse (and of course also of the THz pulse generated from this current pulse) will always have a constant phase of ϕ or $\phi+\pi$, depending on the direction of current flow, but not a value in between. Moreover, if the amplitudes of the hh and lh currents are identical, the overall current will be zero. This theoretical behavior is clearly not in line with the experimental observations. The amplitude and phase spectra of Fig. 3 can only be explained with two superimposed current pulses of identical shape that are temporally delayed with respect to each other or with two superimposed current pulses with different temporal shapes. The latter is illustrated in the right-hand side part of Fig. 4(b) in which the hh current is assumed to decay with a longer time constant compared to the lh current. In this case the shape of the resulting current pulse depends on the ratio of the two current amplitudes and differs from the shape of the hh and lh currents. As a consequence, also the phase of the spectral maximum of the THz traces emitted from the resultant current pulse depends on the ratio of the two current amplitudes and may show a continuous phase variation if this ratio is changed. Moreover, the amplitude of the resulting pulse will only be zero if the amplitudes of the hh and lh current pulses are zero, too. This is exactly what we see in Figs. 3(a) and 3(b) for the excitation of exciton transitions, giving evidence that exciton-driven shift currents do not directly follow the optical pulse envelope but also contain a noninstantaneous contribution. At the moment we can only speculate about the reason for this noninstantaneous contribution. Our observation might confirm a theoretical work[22] where it is shown that the macroscopic polarization of shift currents decays due to intraband scattering in the valence band, which is known to be different for light and heavy holes.

In Fig. 3(b) the spectral dependence of the phase of the THz traces emitted from *xyy* shift currents (empty triangles) is also shown. In principle we would expect to observe a phase shift of the *xyy* shift current signal at the lh-*X* energy.[13] Yet the *xyy* shift current resulting from the QW region of our sample is superimposed on the *xyy* shift current signal from the underlying bulk substrate. Since less than 50% of the excitation light is absorbed in the QW region,[14] the *xyy* signal is dominated by the current response resulting from the bulk substrate. We conclude that the contribution from the bulk GaAs prevents the observation of a pronounced phase shift and excitonic characteristics of the *xyy* shift current.

Finally, we address the spectral dependence of the *xxx* shift current amplitude shown in Fig. 3(a) in more detail. From a comparison with the PLE data of the undoped sample (see Fig. 1), it is evident that the spectral behavior of the amplitude of the *xxx* shift current differs substantially from the absorption spectrum. The most surprising features in the current spectrum are the dip at 1.52 eV and the strong current enhancement at the lh-*X*. The ratio of the THz amplitudes at 1.52 eV and at the energy of the lh-*X* is ~0.07, whereas the ratio of the PLE signals at the same energies is ~0.7 and, thus, an order of magnitude larger. We attribute the difference between the absorption and the current spectrum partially to the fact that contributions from heavy-hole and light-hole transitions are superimposed differently: The overall absorption corresponds to absorption involving electron-heavy-hole transitions *plus* absorption involving electron-light-hole transitions. In contrast, the overall shift current is determined by the heavy-hole contribution *minus* the light-hole contribution. Moreover, it is likely that different temporal dynamics of heavy- and light-hole currents and the complex band structure, e.g., valence band mixing effects, also influence the current spectrum.

In summary, we have provided convincing evidence for an additional shift current tensor element that results from symmetry reduction in GaAs/AlGaAs QWs. Thus shift current measurements allow one to obtain insight into symmetry properties of semiconductor nanostructures in a noninvasive way. Spectrally resolving the current signals resulting from the additional tensor element, we were able to distinguish between heavy- and light-hole currents. Our measurements also show that shift current experiments are a sensitive probe of Coulomb enhancement effects.

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