Optical generation of polarized photoluminescence from GaAs(100)

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Polarized photoluminescence from GaAs(100) was generated using shaped ultrashort laser pulses. A train of three pulses separated by an integer multiple of the longitudinal optical phonon period produced p-polarized continuum emission, whereas trains with half-integer multiples of the phonon period as well as single Gaussian pulses produced s-polarized emission. The p-polarized emission is attributed to recombination of carriers in the L-valley, resulting from plasma generation and coherent phonon-excitation by the pulse train, whereas the s-polarized emission is caused by reflection by the melted surface of unpolarized plasma emission. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3698469]

Polarization of light emitted by carrier recombination in a semiconductor is a sensitive indication of localized structural asymmetry.[1] Photoluminescence (PL) from single semiconductor nanowires has been found to be strongly polarized along the cylindrical axis.[2] The observation of this effect for nanowires with zincblende (ZB) structures, for which dipole selection rules play no role, shows that polarization may be caused by the mismatch between the dielectric constant of the crystal and its surroundings.[3] The switch in polarization direction when the crystal structure is changed from wurtzite to ZB, however, shows that both optical selection rules[4] and dielectric asymmetry[3,5,6] may contribute to the polarization. Structural asymmetry produced by vertically stacking layers of quantum dots also produces polarized PL, which is attributed to quantum confinement.[7] Asymmetry may also be induced by stress caused by mismatch between the coefficient of thermal expansion of a nanostructure and its substrate, producing selective and local control of PL polarization.[8]

In all the examples cited above, polarization results from structural asymmetry of the crystal, in the absence of which unpolarized emission is expected. Here we investigate what effect the directional properties of laser driven electrons have on the PL produced by recombining carriers. We show that asymmetry produced by laser excitation can lead to polarized emission in an otherwise isotropic medium. The ability to control the polarization of the PL by an all-optical method is an important step in the development of sub-ps switches used in applications of plasma photonics.[9]

This study is part of a broader inquiry as to how coherent radiation may be used to control carrier recombination in a semiconductor. The key results from our previous work are summarized in Fig. 1. The solid curve shows the emission produced by a single Gaussian pulse from a Ti:Sapphire laser (805 nm, 62 fs pulse width) focused onto a GaAs(100) crystal in air. The spectrum consists of a pair of lines, produced by fluorescing Ga atoms in the laser-generated plume, riding on top of a broad continuum. Essentially the same spectrum (blue squares) is produced by a series of three pulses spaced by a half-integer multiple of the longitudinal optical phonon period, τ (114 fs at room temperature). If the spacing is an integer multiple of τ, however, a new band appears (red circles), extending from 390 to 460 nm. The red edge of this band corresponds to a direct L-valley conduction→valence band transition. The inset in Fig. 1 shows the signal produced at a fixed wavelength as a function of pulse spacing. The peaks correspond to integer multiples of the optical phonon period, out to 11τ. Finally, we showed that the enhancement of the signal produced by the pulse train is a sensitive function of the phase of the first and third pulses relative to that of the central one, indicating that at least some part of the excitation mechanism is coherent.[10,11]

Our central hypothesis is that trains of ultrashort laser pulses resonant with the optical phonon frequency of a crystal may induce large amplitude oscillations, which in turn

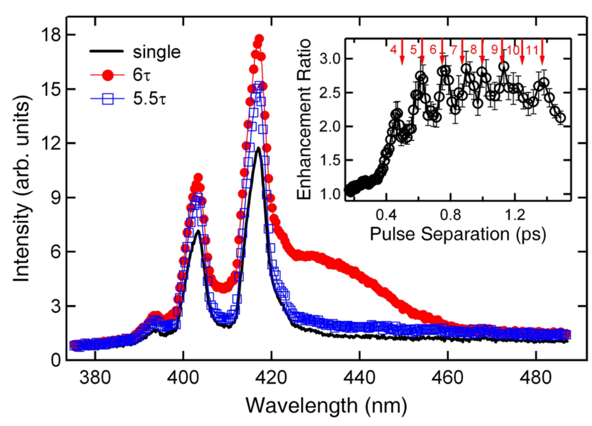

FIG. 1. Photoluminescence from GaAs(100). The solid curve is the spectrum obtained with a single Gaussian shaped pulse. The blue squares and red circles show the spectra obtained with a train of three pulses spaced by 5.5τ and 6τ, respectively. The two intense peaks correspond to a spin-orbit split pair of transitions of neutral Ga, namely $^2P^0_{1/2} \leftarrow {}^2S_{1/2}$ at 403.3 nm and $^2P^0_{3/2} \leftarrow {}^2S_{1/2}$ at 417.2 nm. The inset shows the signal at a wavelength of 450.8 nm as a function of the spacing between the pulses (reproduced from Ref. 10).

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may selectively scatter the carriers.[10,11] A single laser photon exceeds the band gap of GaAs, and two photons provide sufficient energy to overcome the barrier separating the Γ- and L-valleys in the conduction band. In our proposed mechanism, electrons driven by the normal component of the electric field of the laser excite the phonons coherently when the pulse spacing is an integer multiple of τ. The driven phonons in turn transfer momentum to the carriers along the $\Gamma - L$ direction. Because bulk GaAs has a ZB structure, structural effects alone should not polarize the emission.

As in our previous experiments, the crystal is mounted on a motorized 3D stage, which moves the sample so that a fresh surface is exposed to each laser shot. Trains of pulses individually $\sim$150fs wide are generated from a 62 fs transform-limited pulse, using a 640 pixel spatial light modulator with a resolution of 0.14 nm/pixel, employing only phase modulation. The laser beam is p-polarized (i.e., in the incident plane), except where indicated otherwise and is focused onto the sample with a 0.25 NA microscope objective, at an angle 30° from the normal. The resulting PL is collected by a 50.8 cm focal length lens in a direction normal to the laser beam, focused onto the entrance slit of a 0.25 m monochromator, and detected by a photomultiplier that is blind at 800 nm. The laser fluence and intensity at the surface are 27 J/cm^2 and 4.3×10^{13} W/cm^2, respectively, for both the single pulse and the pulse train. This value is well above the damage threshold of the crystal,[13] as is evident from the laser-induced breakdown spectrum produced by the single pulses in Fig. 1. The phonon structure displayed in the insert to Fig. 1 must therefore result from the locally intact lattice beneath the molten surface during the first few ps. In the present experiment, a Glan laser polarizer (Thorlabs) was inserted before the entrance slit of the monochromator. The transmitted PL was recorded at 20° intervals of the polarizer angle, θ, with 15 shots averaged at each position of the polarizer.

The experimental results are shown in Fig. 2. Each panel shows the signal vs. polarizer angle for a single Gaussian-shaped pulse (lowermost trace in each panel), three pulses with a half-integer τ spacing (middle trace), and three pulses with a 6τ spacing. Panels (a) and (b) show the results for two different wavelengths in the continuum (451 and 436 nm), while panels (c) and (d) correspond to the two discrete lines (403 and 417 nm). The curves are least squares fits of the Malus function

$$I(\theta) = A + B\cos^2(\theta - \theta_0), \tag{1}$$

where θ_0 is an instrumental parameter. In all instances, the PL produced by single pulses and half-integer pulse trains is s-polarized. For the resonant (6τ) case, however, opposite behavior is seen for the continuum and discrete wavelengths, with the former giving p-polarized emission and the latter s-polarized emission.

The polarization produced by a single pulse is a general phenomenon observed in the laser ablation of various materials with both fs (Refs. 12 and 14) and ns (Refs. 15 and 16) pulses. Although originally it was thought that the polarization is caused by an alignment effect in the plasma, more recent work showed that the most likely mechanism is reflection of the emission from an unpolarized plasma by the molten surface.[17] The emission is s-polarized because of preferential reflection of that component, as predicted by the Fresnel equations. The maximum polarization is $<50\%$

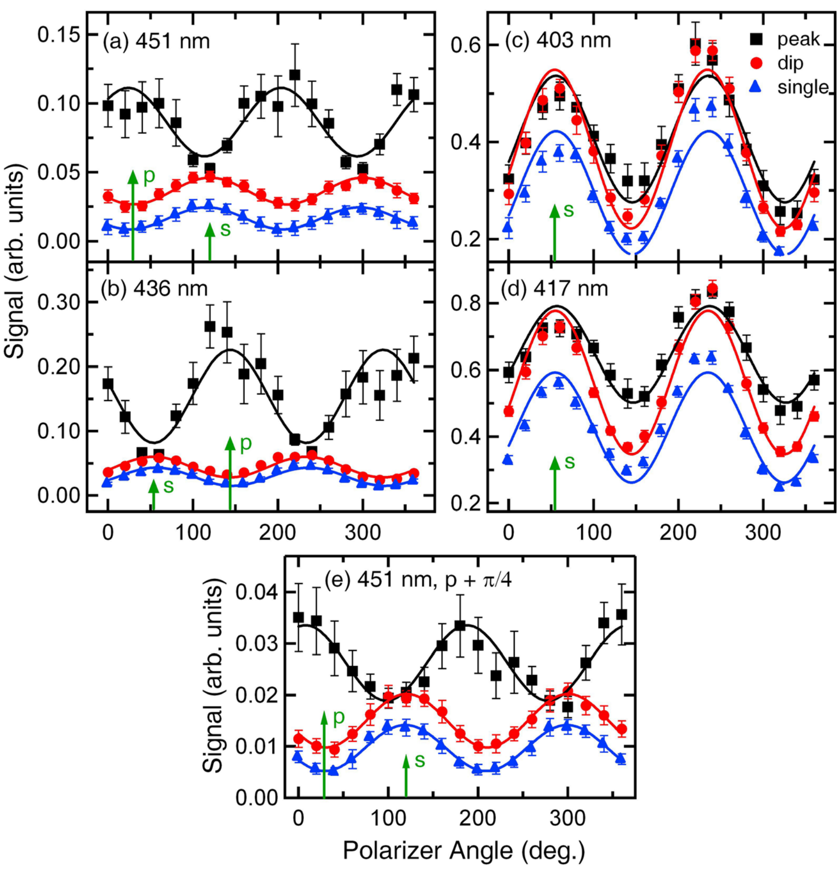

FIG. 2. Transmitted signal vs. polarizer angle. The panels correspond to different emission wavelengths, as indicated. The points labeled "peak" (black squares), "dip" (red circles), and "single" (blue triangles) refer to laser pulses with spacing of 6τ, half-integer τ (9.5τ in panel (a) and 6τ in panels (b)–(e)), and a single Gaussian pulse, respectively. The laser is p-polarized in panels (a)–(d) and polarized at p+π/4 in panel (e). Error bars are twice the standard error for 15 measurements per point.

because at least half of the light reaches the detector directly. In contrast, the p-polarization produced by the 6τ pulse train is characteristic of the phonon-mediated emission. We will return to the origin of this effect later.

To determine the amount of p-polarization produced by the resonantly excited phonons, it is necessary to correct for the s-polarized background caused by laser ablation of the surface. In general, the magnitude of the polarization calculated from a Malus plot is given by

$$P = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} = \frac{B}{2A + B}. \quad (2)$$

Setting the value of θ_0 so that $\theta = 0$ corresponds to p-polarization and $\theta = \pi/2$ corresponds to s-polarization, the transmission of the polarizer may be written as

$$I(\theta) = C[(1-P)/2 + P\cos^2\theta], \quad (3)$$

where the first term results from the polarized component of the electric field and the second term from the unpolarized component. In this equation, $0 \le P \le 1$ corresponds to p-polarized light, $-1 \le P \le 0$ corresponds to s-polarized light, and $C = 2A + B$. Adding the intensities of N beams, each with polarization P_i and amplitude C_i, produces a resultant beam with polarization P_{N+1} and amplitude C_{N+1},

$$P_{N+1} = \sum_{i=1}^{N} f_i P_i \quad (4)$$

$$C_{N+1} = \sum_{i=1}^{N} C_i, \quad (5)$$

where $f_i = C_i/C_{N+1}$.

We model our data by treating the signal produced with a resonant pulse train, I_3, as the sum of a background signal, I_1, produced by a single pulse, and an additional component, I_2, that includes both resonant and non-resonant enhancement of the continuum. We calculate the values of P_2 and C_2 from the measured quantities P_1, C_1, P_3, and C_3, which satisfy the relations $P_2 = (P_3 - C_1 P_1)/C_2$ and $C_2 = C_3 - C_1$. The results are listed in Table I. Several conclusions may be drawn from this analysis. (1) A single pulse produces 40%–50% s-polarized emission regardless of wavelength. (2) Continuum emission (451 and 436 nm) produced by a resonant (6τ) pulse train is p-polarized with $P_2 = 50-70\%$ and $f_2 = 0.6-0.8$. The latter figure indicates that most of the signal is caused by resonant enhancement. (3) Discrete line emission produced by a resonant pulse train (417 and 403 nm) has $P_2 \approx 0$, with $f_2 = 0.3-0.5$. The fact that the emission is not s-polarized and that f_2 is not zero indicates that the underlying continuum at these wavelengths is partially p-polarized by the laser excitation. This observation is consistent with the structureless envelope of the L-valley emission (see Fig. 2(b) of Ref. 10). (4) Continuum emission produced by a non-resonant pulse train (417 and 403 nm) also has $P_2 \approx 0$, with $f_2 = 0.3-0.5$. The fact that in this case the emission is not s-polarized and that f_2 is not zero indicates that some recombination in the L-valley occurs even without resonant phonon excitation. This inference is consistent with the observation that the modulation depth is only 25% in the inset of Fig. 1 and in general was never found to exceed 50%.[10] (5) Discrete line emission produced by a non-resonant pulse train is s-polarized with $P_2 \approx 40\%$ and $f_2 = 0.35-0.4$. In this case, the combination of mostly discrete line emission, produced by recombination of ions and electrons in the plume, and the non-resonant nature of the pulse train results in surface reflection being the exclusive source of polarized emission.

TABLE I. Polarization components.[a]

λ (nm)[b]	P_1	P_2	P_3	f_2	Pulse spacing
451 (c)	-0.48 ± 0.04	$+0.47\pm0.04$	$+0.29\pm0.03$	0.81	6τ
		-0.07 ± 0.26	-0.26 ± 0.13	0.54	9.5τ
436 (c)	-0.49 ± 0.04	$+0.69\pm0.07$	$+0.47\pm0.04$	0.81	6τ
		-0.13 ± 0.12	-0.35 ± 0.03	0.34	5.5τ
417 (d)	-0.39 ± 0.04	$+0.10\pm0.09$	-0.22 ± 0.02	0.34	6τ
		-0.37 ± 0.10	-0.38 ± 0.02	0.26	5.5τ
403 (d)	-0.43 ± 0.04	-0.03 ± 0.16	-0.32 ± 0.03	0.27	6τ
		-0.41 ± 0.03	-0.42 ± 0.13	0.23	5.5τ
451 (c)	-0.46 ± 0.04	$+0.70\pm0.05$	$+0.27\pm0.03$	0.63	6τ, p+ $\pi/4$
		-0.14 ± 0.05	-0.35 ± 0.01	0.35	5.5τ, p+ $\pi/4$

[a]Positive P denotes p-polarization, and negative P denotes s-polarization.
[b]*c* and *d* denote wavelengths of the continuum and discrete lines, respectively.

The principle mechanisms for coherent phonon excitation in semiconductors are either displacive or impulsive in character.[18,19] In the case of polar semiconductors such as GaAs, it is well established that the dominant mechanism is a displacement of the surface charge.[20] In the present experiment, however, melting of the surface layer by the early part of the pulse train diminishes the effect of surface Fermi level pinning and the depletion field. Instead, we have proposed that ballistic electrons generated by the laser penetrate the electron-hole plasma in the unmelted crystal and excite the lattice directly. It is also possible that plasmons excited by the laser couple to the phonons.[21] For resonant excitation of the plasma to occur, it is necessary that the electric field of the laser have a component normal to the surface.[22] By interacting with the gradient of the plasma normal to the surface, the electromagnetic wave generates longitudinal electrostatic waves in the plasma. This mechanism is supported by our observation that the phonon oscillations are strongest for a p-polarized laser beam and vanish entirely if the laser beam is s-polarized or if it is incident close to the surface normal (Figs. 4(a) and 4(b) of Ref. 10). Here we tested the mechanism further by measuring the polarization of the PL generated by exciting the sample with light linearly polarized at $\theta_0 = \pi/4$ (i.e., half way between s and p). The result is shown in Fig. 2(e) and at the bottom of Table I. We find that although the resonant enhancement is lower than for p-polarization ($f_2 = 0.6$), the P values are comparable. In particular, the observation that the PL is p-polarized shows that it is the normal component of the electric field that determines the polarization of the outgoing photons.

We consider two possible mechanisms for the p-polarized PL. One is an "active" mechanism in which the local electric field of the excited LO phonons produces an asymmetry and leads to the alignment of the electron-hole pair dipoles during recombination. In effect, it is the p-polarized laser source (in the form of trains of pulses with spacings of integer multiples of τ) that provides the optical field and frequency necessary for exciting the LO phonons, the field of which in turn serves to create an asymmetry in the dipole emission from recombining electron-hole pairs. An alternative is a "passive" mechanism in which free electrons on the surface of the material have greater conductivity along the surface as compared to the normal and therefore preferentially absorb the s-component of the PL. This mechanism provides a uniform explanation of the s-polarized background and the p-polarized resonantly excited continuum. In both cases the surface acts as filter, namely a reflective filter for plasma-born emission and a transmission filter for PL produced within the crystal.

Understanding and controlling the polarization of photoluminescence is important in areas such as solid state illumination and optimization of solar photovoltaic cells. Previous studies concentrated on the effects of structural asymmetry on the polarization of the emitted light. Here we have shown that by shaping the phase of the light source used to excite the carriers, it is possible to control not only the frequency but also the polarization of the photoluminescence. Polarization of the total emission exceeding 30% was readily achieved, and it is anticipated that still greater polarization may be obtained with optimized pulse shapes.[11]

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[1]V. Zwiller, L. Jarlskog, M. Pistol, C. Pryor, P. Castrillo, W. Seifert, and L. Samuelson, Phys. Rev. B **63**, 233301 (2001).
[2]W. Wang, M. S. Gudiksen, X. Duan, Y. Cui, and C. M. Lieber, Science **293**, 1455 (2001).
[3]T. B. Hoang, A. F. Moses, L. Ahtapodov, H. Zhou, D. L. Dheeraj, A. T. J. van Helvoort, B. Fimland, and H. Weman, Nano Lett. **10**, 2927 (2010).
[4]R. Venugopal, P. I. Lin, C. C. Liu, and Y. T. Chen, J. Am. Chem. Soc. **127**, 11262 (2005).
[5]A. Mishra, L. V. Titova, T. B. Hoang, H. E. Jackson, L. M. Smitha, J. M. Yarrison-Rice, Y. Kim, H. J. Joyce, Q. Gao, H. H. Tan, and C. Jagadish, Appl. Phys. Lett. **91**, 263104 (2007).
[6]C. X. Shan, Z. Liu, and S. K. Hark, Phys. Rev. B **74**, 153402 (2006).
[7]T. Inoue, M. Asada, N. Yasuoka, O. Kojima, T. Kita, and O. Wada, Appl. Phys. Lett. **96**, 211906 (2010).
[8]O. Moshe, D. H. Rich, B. Damilano, and J. Massies, Appl. Phys. Lett. **98**, 061903 (2011).
[9]H. Wen, D. Daranciang, and A. M. Lindenberg, Appl. Phys. Lett. **96**, 161103 (2010).
[10]Z. Hu, S. Singha, and R. J. Gordon, Phys. Rev. B **82**, 115204 (2010).
[11]S. Singha, Z. Hu, and R. J. Gordon, J. Phys. Chem. A **115**, 6093 (2011).
[12]Y. Liu, S. Singha, T. E. Witt, and R. J. Gordon, Appl. Phys. Lett. **93**, 161502 (2008).
[13]L. Huang, J. P. Callan, E. N. Glezer, and E. Mazur, Phys. Rev. Lett. **80**, 185 (1998).
[14]J. S. Penczak, Jr., Y. Liu, and R. J. Gordon, J. Phys. Chem. A **113**, 13310 (2009).
[15]Y. Liu, J. S. Penczak, Jr., and R. J. Gordon, Opt. Lett. **35**, 112 (2010).
[16]E. Majd, A. S. Arabanian, R. Massudi, Opt. Lasers Eng. **48**, 750 (2010).
[17]J. S. Penczak, Jr., Y. Liu, R. D. Schaller, D. H. Rich, and R. J. Gordon, "The Mechanism for Continuum Polarization in Laser Induced Breakdown Spectroscopy of Si(111)," Spectrochimica Acta B (to be published).
[18]T. Dekorsy, C. C. Cho, and H. Kurz, *Topics of Applied Physics* (Springer, Berlin, Heidelberg, 2000), Vol. 76.
[19]G. A. Garrett, T. F. Albrecht, J. F. Whitaker, and R. Merlin, Phys. Rev. Lett. **77**, 3661 (1996).
[20]K. J. Yee, Y. S. Lim, T. Dekorsy, and D. S. Kim, Phys. Rev. Lett. **86**, 1630 (2001).
[21]A. V. Kuznetsov and C. J. Stanton, Phys. Rev. B **51**, 7555 (1995).
[22]S. C. Wilks and W. L. Kruer, IEEE J. Quantum Electron. **33**, 1954 (1997).