Influence of surface passivation on ultrafast carrier dynamics and terahertz radiation generation in GaAs

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The carrier dynamics of photoexcited electrons in the vicinity of the surface of $(NH_4)_2S$-passivated GaAs were studied via terahertz emission spectroscopy and optical-pump terahertz-probe spectroscopy. Terahertz emission spectroscopy measurements, coupled with Monte Carlo simulations of terahertz emission, revealed that the surface electric field of GaAs reverses after passivation. The conductivity of photoexcited electrons was determined via optical-pump terahertz-probe spectroscopy and was found to double after passivation. These experiments demonstrate that passivation significantly reduces the surface state density and surface recombination velocity of GaAs. Finally, it was demonstrated that passivation leads to an enhancement in the power radiated by photoconductive switch terahertz emitters, thereby showing the important influence of surface chemistry on the performance of ultrafast terahertz photonic devices. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2398915]

Surface and interface states can dominate charge carrier transport in semiconductors, for instance creating unexpectedly high mobilities in nanometer-thick silicon-on-insulator structures[1] or significant carrier trapping in polymer field-effect transistors.[2] Marked improvements in the performance of macroscopic III–V devices can be obtained by chemical treatments that remove the surface oxide layer and passivate the semiconductor/air interface electrically and chemically.[3,4] Typically, passivation prevents electrons from surface atoms forming defect states within the semiconductor's band gap,[5] thereby reducing the surface recombination rate. Passivation techniques have led to performance enhancements for III–V laser diodes,[6] solar cells,[7] and bipolar transistors.[3] However, discussion of passivation with regard to sources of terahertz radiation has been limited to Schottky diode multipliers,[8] which produce continuous wave radiation at typically <300 GHz. Surface states may also be expected to play an important role in broadband emitters of terahertz radiation,[9,10] where the photoexcited carrier distribution lies within ~ 1 μm of the surface.

In this letter we report an investigation into carrier recombination at $(NH_4)_2S$-passivated GaAs surfaces using time-resolved spectroscopy and show how this knowledge of carrier dynamics can be used to improve the performance of pulsed terahertz emitters. Three complementary techniques were used in this study: (i) *Surface terahertz emission*, which is an excellent probe of the space-charge induced electric field at the surface of bulk semiconductors, owing to a strong sensitivity to the bulk doping level;[11] (ii) *optical-pump terahertz-probe spectroscopy*, which allows the conductivity of photocarriers in a semiconductor to be measured as a function of time after photoexcitation[12,13] (as the electron lifetime and mobility can be determined using this technique, we are thus able to optimize materials for specific device applications); (iii) *terahertz emission from photoconductive switch devices*, which we use as an example of how controlling the dynamics of charge carriers in the vicinity of a surface, in particular by surface passivation, can be used to improve significantly the performance of terahertz devices.

The surfaces of samples of semi-insulating (SI) GaAs and InSb [both with (100) orientation, with dark resistivities of 1.5×10^{8} and 1.2×10^{-1} Ω cm, respectively] were etched with 5:1:1 H_2SO_4:H_2O_2:H_2O and subsequently passivated by dipping in $(NH_4)_2S$ for 10 min.[4] A reference set of samples was made from the same wafers, without the passivation step, and was allowed to oxidize completely in air.

We used terahertz time-domain spectroscopy[14] to measure the terahertz emission from passivated and etched samples of GaAs and InSb, in a setup similar to that of Ref. 15. 90% of the output of a Ti:sapphire oscillator laser (10 fs pulse duration, 75 MHz repetition rate, 450 mW beam power, 790 nm wavelength) was used to generate carriers in the sample; the remainder was used to detect the emitted terahertz transients using electro-optic sampling [with a 0.2 mm (110) ZnTe crystal on a 6 mm (100) ZnTe substrate].

Terahertz emission from semiconductor surfaces can be used to investigate the carrier dynamics in ion-damaged semiconductors,[15] or to probe the surface charge distribution. At the typical pump fluences available with unamplified Ti:sapphire lasers, the dominant terahertz radiation mechanism in (100) GaAs is charge separation under the surface field,

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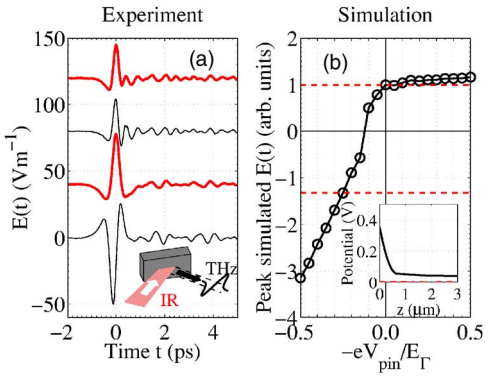

FIG. 1. (Color online) (a) From bottom to top: Emitted time-domain terahertz electric field from surfaces of etched GaAs, passivated GaAs, etched InSb, and passivated InSb—the etched samples act as references. The peak of terahertz pulses emitted from InAs (not shown) was +550 V m^{-1}. The oscillations after the main pulse result from the terahertz absorption lines of atmospheric water vapor. Passivation produces no noticeable change in E_{THz} for InSb but causes the polarity to flip and the amplitude to decrease for GaAs. Inset: Schematic of experimental geometry showing the infrared (IR) emitter pump beam at 45° to the emitter and the radiated terahertz pulse. (b) Peak of simulated terahertz electric field emission from GaAs surfaces vs surface pinning potential energy eV_{pin} relative to the band gap energy E_Γ =1.42 eV. Dotted horizontal lines represent the relative measured peak fields for the passivated (top) and etched reference (bottom) samples. Inset: Simulated electrostatic potential 50 fs after the arrival of the infrared pump pulse as a function of depth z into the semiconductor for V_{pin}=0.355 V (solid line) and V_{pin}=0 V (dashed line).

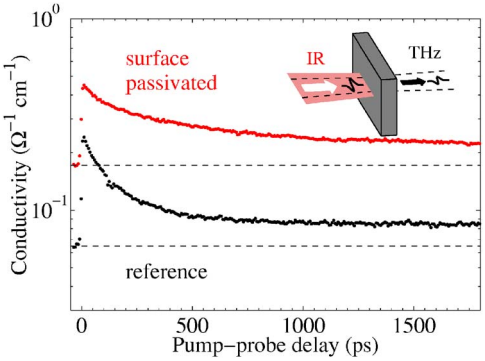

FIG. 2. (Color online) Time-resolved conductivity of passivated (top) and reference (bottom) GaAs samples as measured via optical-pump, terahertz-probe spectroscopy. The dotted lines indicate a nonzero conductivity before the pump pulse arrives, owing to the bulk lifetime (τ_b=15 ns) exceeding the repetition period between laser pulses (13.3 ns). Inset: Schematic of experimental geometry showing the IR sample pump beam and the incident and transmitted terahertz-probe pulse.

while for higher mobility semiconductors such as (100) InAs it is the photo-Dember effect[11] (the difference in electron and hole mobilities). At higher fluences, and for (110) and (111) crystal cuts, terahertz emission from optical rectification becomes significant.[16]

The terahertz emission from the surfaces of the passivated and reference samples was measured and is shown in Fig. 1(a). The polarity of the terahertz electric field from the etched GaAs sample was opposite to that of InAs (not shown), while for passivated GaAs the radiated pulses had the same polarity as InAs. The polarity change suggests that passivation suppresses the surface states that create the surface field, namely that passivated GaAs acts as a photo-Dember emitter. No significant change in the terahertz emission from samples of InSb was observed after applying the same passivation process, since InSb (like InAs) is primarily a photo-Dember emitter (Fig. 1).[16]

We have used a three-dimensional carrier dynamics simulation[11] to investigate how changes to the surface states in GaAs alter terahertz emission. The influence of surface defects can be described by the pinning of the electrostatic potential at the surface, where the potential relative to the bulk is V_{pin}. Figure 1(b) indicates the peak of the simulated terahertz electric field as a function of V_{pin}. With no Fermi level pinning (V_{pin}=0) the simulated terahertz radiation has the same sign as InAs, and the semiconductor acts as a photo-Dember emitter—there is no surface field, as the inset to Fig. 1(b) indicates. As V_{pin} becomes increasingly negative the simulated field strength changes in sign, owing to the surface field component. Therefore, assuming that the passivated GaAs sample has V_{pin}=0, the pinning potential in the etched sample can be estimated from the relative emission amplitudes as $V_{pin} \leqslant -0.25E_\Gamma/e$=0.355 V.

In order to investigate the dynamics of photoexcited carriers close to surface defects we measured the time-resolved conductivity $\sigma(t')$ of the passivated and etched GaAs samples. The experimental geometry used was as follows: 45% of the laser's output was used to generate terahertz pulses from a SI-GaAs photoconductive switch[14] and 10% to detect the transient after transmission through the sample. The remaining 45% of the beam was used to photoexcite the sample collinearly—this sample pump beam was mechanically chopped at 160 Hz. The change in the transmitted terahertz electric field induced by the pump was recorded as a function of the arrival time t' of the sample pump pulse relative to the terahertz pulse.

The time-resolved conductivity $\sigma(t')$ was readily obtained from these data[17] and is shown in Fig. 2. At zero pump-probe delay time (t'=0) the conductivity increases rapidly owing to the photogeneration of electrons. The decay in conductivity is nonexponential: at early delay times surface recombination significantly depopulates the electron concentration, while at later delay times ($\gtrsim$600 ps) the carrier distribution has had time to diffuse into the bulk, reducing the role of surface recombination.[17] It can be seen that the surface passivated sample has a larger initial conductivity than the etched sample and a longer initial decay time constant. As the incident photon flux was identical for the two samples, this increase in conductivity can be attributed to a 1.9× larger initial electron mobility μ. An exponential fit to the initial decay (up to 40 ps) produces a time constant of τ=389 ps for the passivated sample, twice that of the etched sample (τ=192 ps). We observed a comparable enhancement in conductivity using $Na_2S \cdot 9H_2O$ to passivate the surface of GaAs.[4]

Sulfur passivated GaAs is known to be partially unstable in oxygen—indeed after storing a sample in air for 2 days we measured a 9% drop in peak conductivity. The deposition of a thin layer of silicon nitride after sulfur passivation may prevent the degradation of the sulfur-treated GaAs surface.[18,19] The effect of this degradation was minimized during these experiments by storing samples in a nitrogen glove box.

We modeled the nonexponential shape of the decay in σ using a solution to the one-dimensional diffusion equation[17] in order to obtain the surface recombination velocity S_0. With a bulk lifetime τ_b=15 ns (taken from the limit of the decay in Fig. 2) good agreement is found with the measured σ when

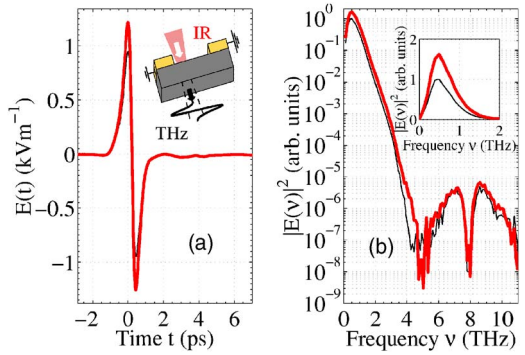

FIG. 3. (Color online) (a) Electric field strength of emitted terahertz pulses from 400 μm gap photoconductive switches made on passivated GaAs (thick line) and an etched reference (thin line) as a function of electro-optic delay time. Inset: Schematic of experimental geometry showing the IR emitter pump beam close to the anode contact of the photoconductive switch and the radiated terahertz pulse. (b) Power spectra of terahertz emission from passivated (thick line) and etched (thin line) GaAs obtained by Fourier transforming the data in (a). These data are shown on a linear scale in the inset.

$S_0=1.2\times10^6$ cm s^{-1} for the etched reference and $S_0=2.0\times10^5$ cm s^{-1} for the surface passivated sample. These values correspond well to those in the literature for etched and passivated GaAs surfaces (however, S_0 can be reduced further to $S_0=10^3$ cm s^{-1} by alternative surface treatments[4]). The Shockley-Read-Hall model predicts that $S_0=n_t v\Sigma$ for a surface areal trap density n_t, scattering cross-section Σ, and carrier velocity v. Assuming that v and Σ are identical before and after passivation, n_t for the passivated sample is 17% of that in the etched sample. The passivation step can therefore directly be seen to produce a surface with fewer recombination centers.

At large pump-probe delay times ($\gtrsim$1000 ps) the decay in conductivity slows, as the carrier distribution has diffused into the bulk. The bulk lifetime exceeds the repetition period between laser pulses (13.3 ns), resulting in a nonzero conductivity at negative pump-probe delays.

The terahertz emission from large-area photoconductive switches fabricated on passivated and etched GaAs is reported in Fig. 3. It can be seen that the peak terahertz electric field strength from the passivated sample is larger than that of the etched reference, with a near doubling of the emitted power [Fig. 3(b)]. This increase is due to the larger change in conductivity σ of the passivated sample (owing to its greater mobility), since the emitted terahertz electric field is $E_{\mathrm{THz}}\propto\partial J/\partial t=\partial(\sigma E)/\partial t$, where current density J flows at an applied field E.[11]

The observation that electrons in SI-GaAs can have lifetimes exceeding the pulse period of high repetition rate lasers (Fig. 2) is of significance to photoconductive terahertz emitters and detectors. The residual carriers created by the preceding laser pulse will reduce the change in conductivity and therefore also the emitted field strength. In addition, the lowering of the dark resistivity increases the noise background and heats the emitter, which can require water cooling when operated at high voltages.[20] Similarly, the noise in photoconductive detectors of terahertz radiation is increased by long-lived electrons in devices fabricated on SI-GaAs and low-temperature grown or ion-damaged layers (thinner than the absorption depth) on semi-insulating substrates.[21]

In conclusion, we have investigated the ultrafast carrier dynamics of passivated GaAs surfaces via time-resolved conductivity measurements, terahertz emission spectroscopy, and simulation. After passivation the terahertz electric field emitted from the GaAs surface flipped in polarity to correspond to that of photo-Dember emitters such as InSb and InAs. This change is indicative of the removal of the surface defects after passivation and was reproduced by carrier dynamics simulations of terahertz emission. Additionally, the mean mobility of photoexcited electrons in $(NH_4)_2S$-passivated GaAs was measured by optical-pump terahertz-probe spectroscopy and was found to be twice that of an unpassivated reference sample. Ensuring a high-quality surface with a low defect concentration was shown to enable improved photoconductive sources of terahertz radiation, as demonstrated by the observation of a power enhancement for photoconductive antenna emitters after passivation. This method can be used in addition to other schemes that increase the power of terahertz sources (such as placing a hemispherical silicon lens to collimate the emitted radiation, or using an anti-reflection coating to enhance coupling from the emitter into free space) and has the benefit of introducing no dispersive media into the terahertz path.

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[1] P. Zhang, E. Tevaarwerk, B. Park, D. Savage, G. Celler, I. Knezevic, P. Evans, M. Eriksson, and M. Lagally, Nature (London) **439**, 703 (2006).
[2] J. Lloyd-Hughes, T. Richards, H. Sirringhaus, E. Castro-Camus, L. M. Herz, and M. B. Johnston, Appl. Phys. Lett. **89**, 112101 (2006).
[3] C. Sandroff, R. Nottenburg, J. Bischoff, and R. Bhat, Appl. Phys. Lett. **51**, 33 (1987).
[4] E. Yablonovitch, C. Sandroff, R. Bhat, and T. Gmitter, Appl. Phys. Lett. **51**, 439 (1987).
[5] V. Bessolov and M. Lebedev, Semiconductors **32**, 1141 (1998).
[6] S. Kamiyama, Y. Mori, Y. Takahashi, and K. Ohnaka, Appl. Phys. Lett. **58**, 2595 (1991).
[7] M. Mauk, S. Xu, D. Arent, R. Mertens, and G. Borghs, Appl. Phys. Lett. **54**, 213 (1989).
[8] H. Hartnagel, V. Ichizli, and M. Rodriguez-Girones, Appl. Surf. Sci. **190**, 428 (2002).
[9] P. Smith, D. Auston, and M. Nuss, IEEE J. Quantum Electron. **24**, 255 (1988).
[10] Y. C. Shen, P. C. Upadhya, E. H. Linfield, H. E. Beere, and A. G. Davies, Appl. Phys. Lett. **83**, 3117 (2003).
[11] M. B. Johnston, D. M. Whittaker, A. Corchia, A. G. Davies, and E. H. Linfield, Phys. Rev. B **65**, 165301 (2002).
[12] M. C. Nuss, D. H. Auston, and F. Capasso, Phys. Rev. Lett. **58**, 2355 (1987).
[13] M. Beard, G. Turner, and C. Schmuttenmaer, J. Appl. Phys. **90**, 5915 (2001).
[14] C. Schmuttenmaer, Chem. Rev. (Washington, D.C.) **104**, 1759 (2004).
[15] J. Lloyd-Hughes, E. Castro-Camus, M. D. Fraser, C. Jagadish, and M. B. Johnston, Phys. Rev. B **70**, 235330 (2004).
[16] P. Gu, M. Tani, S. Kono, K. Sakai, and X. Zhang, J. Appl. Phys. **91**, 5533 (2002).
[17] M. Beard, G. Turner, and C. Schmuttenmaer, Phys. Rev. B **62**, 15764 (2000).
[18] S. Shikata and H. Hayashi, J. Appl. Phys. **70**, 3721 (1991).
[19] W. S. Hobson, U. Mohideen, S. J. Pearton, R. E. Slusher, and F. Ren, Electron. Lett. **29**, 2199 (1993).
[20] G. Zhao, R. N. Schouten, N. van der Valk, W. T. Wenckebach, and P. C. M. Planken, Rev. Sci. Instrum. **73**, 1715 (2002).
[21] A. Hussain and S. Andrews, Appl. Phys. Lett. **88**, 143514 (2006).