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Improved Performance of GaAs-Based Terahertz Emitters via Surface Passivation and Silicon Nitride Encapsulation

Carl Headley, Lan Fu, *Senior Member, IEEE*, Patrick Parkinson, Xinlong Xu, James Lloyd-Hughes, Chennupati Jagadish, *Fellow, IEEE*, and Michael B. Johnston

***Abstract*—We have improved the stability and performance of terahertz (THz) photoconductive (Auston) switches using a combination of $(NH_4)_2S$ surface passivation (SP) and silicon nitride (Si_3N_4) encapsulation. The influences of SP and encapsulation on the ultrafast electron dynamics in GaAs were examined using THz emission spectroscopy and optical pump–THz probe spectroscopy. The power of THz radiation from the surface of photoexcited GaAs increased by a factor of 5 after passivation and encapsulation, while the process lengthened the trapping time for photoexcited charge carriers. By fabricating and assessing the performance of photoconductive switches, we found that passivation and encapsulation increased the average THz power generated fourfold.**

***Index Terms*—Photoconductive switch (PCS), surface passivation (SP), terahertz (THz), time-domain spectroscopy.**

I. Introduction

One METHOD of generating terahertz (THz) radiation for the technique of THz time-domain spectroscopy (THz-TDS) utilizes photoconductive switches (PCSs) that are illuminated by a pulsed femtosecond laser. In order to maximize the output from a PCS, one may increase the applied electric-bias field and the intensity of the laser beam incident on the PCS. However, in doing so, this may limit the operational lifetime of the PCS [1]. Hence, other methods are sought to maximize the THz radiation output and efficiency of PCSs.

A drawback of using GaAs is that bonds are exposed and left "dangling" after the surface of GaAs has been cleaved [2]. These bonds act as trapping centers for photo-excited charge carriers and therefore reduce the conductivity of the material. One method to counteract this trapping effect involves using sulfur in a surface-passivation (SP) process to bridge the broken covalent bonds on the surface of GaAs [3]. It was demonstrated in [4] that this SP treatment results in an increased THz output power. However, it was found that surface-passivated (SP) GaAs PCS emitters tend to show a degraded performance over time, which was attributed to the oxidation of the treated surfaces under continued exposure to air [4].

One method of preventing surface oxidation is to block the interaction of the sulfur atoms and oxygen by encapsulating the semiconductor with a layer of silicon nitride (Si_3N_4). The effects of SP and encapsulation (or overpassivation) using Si_3N_4 on GaAs have been well studied. Previous studies utilized techniques such as reflection high-energy electron diffraction (RHEED) [5], [6], X-ray photoelectron spectroscopy (XPS) [7], [8], photoluminescence [9]–[11], and capacitance–voltage measurements [12], [13]. Relatively few studies have focused upon the application of SP and encapsulation for the improvement of THz devices.

The work described in this paper was undertaken to ascertain whether a PCS with Si_3N_4 on SP GaAs would result in a higher output power of THz radiation and an enhanced resistance to oxygen. The first part of this paper reports *THz emission* measurements that investigated the properties of the in-built surface electric field. The second section concerns *optical pump–THz probe* (OPTP) spectroscopy to look for any changes in photoconductivity. Finally, the third part covers *THz PCS emission* to ascertain whether THz radiation generated from electrically driven sources is also enhanced using the new encapsulation method.

II. Methods

The samples were all prepared from wafers of semiinsulating (SI) GaAs of approximately 11 mm $\times$ 11 mm square and 0.38 mm thickness. The sample surfaces were first etched with H_2SO_4:H_2O_2:H_2O=5:1:1 for 1 min, then passivated in 20% $(NH_4)_2S$ for 10 min. The Si_3N_4 encapsulation layer (100 nm) was deposited by plasma-enhanced chemical vapor deposition (PECVD) at 100 °C for samples used in THz PCS emission measurements and at 70 °C for samples used in the THz emission and OPTP measurements. The PCS emitters were defined using photolithography and subsequent Ge:Au metalization. Alloyed Ohmic contacts were made by annealing at 380 °C for 1 min. For the SiN encapsulated PCSs a buffered HF etch was used before metalization to remove the Si_3N_4 in the region of the contacts, followed by an etch in 10% HCl to remove the native oxide.

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C. Headley, P. Parkinson, X. Xu, J. Lloyd-Hughes, and M. B. Johnston are with the Clarendon Laboratory, Department of Physics, University of Oxford, Oxford, OX1 3PU, U.K. (e-mail: m.johnston@physics.ox.ac.uk).

L. Fu and C. Jagadish are with the Research School of Physics and Engineering, Australian National University, Canberra, A.C.T. 0200, Australia.

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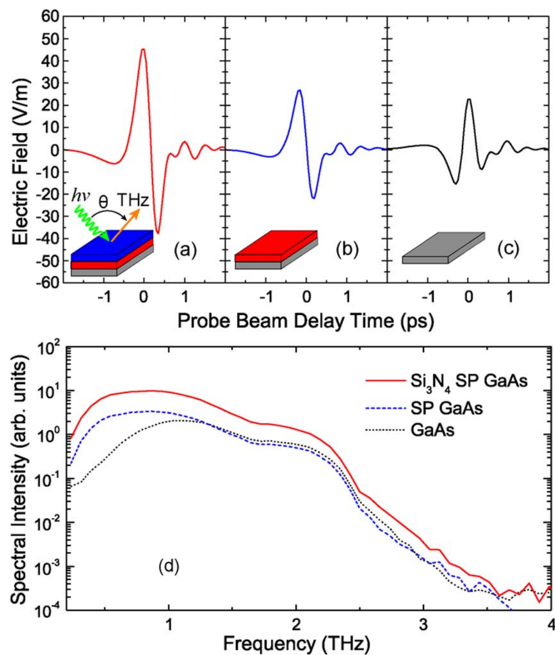

Fig. 1. Surface-emitted electric field of the Si_3N_4 SP GaAs, SP GaAs, and GaAs samples are shown in the main areas of (a), (b), and (c), respectively, with their respective sample geometries shown in the insets (gray = GaAs, red = SP layer, blue = Si_3N_4 layer). (d) Fourier transform of the pulses in (a)–(c). Inset of (a) shows the experimental geometry ($\theta = 90°$). The SP GaAs data were taken approximately 211 days after fabrication.

The thickness of the Si_3N_4 layer was chosen to be 100 nm, so that with a refractive index of $\sim$2 for Si_3N_4 at 800 nm, the layer acts as a $\lambda/4$ antireflection coating from free space into the semiconductor, minimizing the reflectivity. At 800 nm wavelength, the normal-incidence reflectivity from bare GaAs is $\sim$33% without the Si_3N_4 layer, and less than 3% with the film. Since the reflectivity is lower with the encapsulation layer, 30% more carriers should be generated in the GaAs (the absorption of the Si_3N_4 layer is negligible at 800 nm).

The laser used in all experiments was an IR Ti:sapphire laser (Mai Tai, Spectra-Physics) that had an output power of 0.84 W and center wavelength of 800 nm, pulse duration of 100 fs, and a repetition frequency of 80 MHz. The measurements were all taken under vacuum ($\sim$0.1 mbar).

III. THz Surface Emission

THz emission measurements from semiconductor surfaces are sensitive to the space-charge-induced electric field near the surface [14], and hence are an excellent probe of surface chemistry. When a GaAs surface is illuminated with pulses from a femtosecond laser oscillator, the two main mechanisms that contribute to emission of THz radiation are: 1) the acceleration of charge in the surface electric field of the sample and 2) the photo-Dember effect [15]. An effective passivation of the GaAs surface reduces the surface electric field in the depletion region, and therefore, severely reduces the contribution of the first mechanism [4].

In this study, the THz emission from the surface of the samples was collected using a $45°$ reflection geometry [see Fig. 1(a)], with a setup similar to that described in [16], and with an incident beam power of 180 mW. The THz electric field was detected using electro-optic sampling with a (1 1 0) ZnTe detection crystal of 2-mm thickness.

To determine the effect of our SP and encapsulation technique on the surface chemistry of GaAs, we recorded THz emission data from three GaAs samples. Fig. 1(a) shows the electric field transient emitted from a passivated and encapsulated surface, while Fig. 1(b) shows data from a sample that were passivated only. A reference transient from an untreated GaAs wafer is shown in Fig. 1(c). It is important to note that the *polarity* of the THz transient from the passivated samples is opposite to the polarity of the transient emitted from the reference GaAs wafer [see Fig. 1(c)]. This flipping effect is clear evidence that our passivation technique successfully suppresses the states at the surface of GaAs that create the surface electric field, and suggests that passivated GaAs acts more like a photo-Dember emitter than a surface-field THz emitter [4]. In the SP GaAs sample, surface recombination was less substantially suppressed (as the lifetimes reported in Section IV suggest), and both mechanisms are likely to contribute. The relative contributions of surface-field THz emission and photo-Dember emission can be studied computationally via Monte Carlo simulations with different surface pinning energies [4]. Furthermore, the similarity between the transients shown in Fig. 1(a) and (b) confirm that the encapsulation process does not degrade the passivation. The encapsulation does, however, preserve the passivation effect over time.

The spectra calculated from the transients are shown in Fig. 1(d). The spectra of the two passivated samples are similar, while the unpassivated sample exhibits a reduced power at low frequency, presumably as a consequence of the differing emission mechanism. The emitted power from each sample was calculated by integrating the spectra shown in Fig. 1(d) between 0.2 and 4 THz. The Si_3N_4 SP GaAs sample emitted $4.2\times$ the power emitted by the GaAs reference sample, whereas the SP GaAs sample yielded a value $1.7\times$ that of GaAs. The increased power emitted from the encapsulated sample can be explained in terms of the transmission of laser radiation into the sample owing to the lower reflectivity with the SiN layer.

IV. Time-Resolved Photoconductivity

The performance of a THz PCS is to a large part determined by the photoconductivity of the device within a few picoseconds after photoexcitation. Thus, by measuring the conductivity of a material as a function of time, we can not only reveal information about the ultrafast charge carrier dynamics in that material, but we can also assess its suitability as a substrate for fabricating PCSs on. We used OPTP spectroscopy to measure the time-resolved photoconductivity of our samples, which has been used previously to study surface recombination in pristine [17] and passivated [4] bulk semiconductors. In the particular measurements described here, the THz and optical pump (1/e) beam waists were 2.28 and 2.80 mm, respectively, the pump fluence was calculated to be 35 nJ/(cm^2·pulse), and the detector was a (1 1 0) ZnTe crystal of 1 mm thickness.

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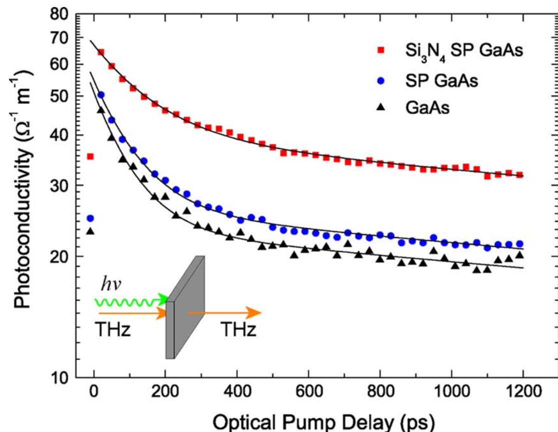

Fig. 2. Measured conductivity of the photoexcited carrier population as a function of time after excitation. The black solid lines show the fittings to the datasets. The inset shows the experimental geometry on a GaAs wafer, the wavy (green) arrow represents the incident optical pump beam at 800 nm and the straight (orange) arrow represents the incident and exiting THz probe beam. The SP GaAs data were taken 311 days after the passivation process.

TABLE I
SURFACE-TRAPPING TIMES OF PHOTOGENERATED ELECTRONS

Sample	τ (ps)
Si_3N_4 SP GaAs	167 ± 2
SP GaAs	116 ± 3
GaAs	106 ± 1

The curves in Fig. 2 show the photoconductivity of each sample (measured at room temperature) as a function of time $\sigma(t')$ after photoexcitation. The photoconductivity data exhibit a double exponential decay: we attribute the shorter time constant to the initial trapping of photogenerated electrons at the surface, and the longer time constant to the recombination of electrons in the bulk GaAs. As our samples were cleaved from the same wafer, the trapping time attributed to bulk GaAs should be identical for all our samples. Therefore, when fitting the data, we applied the constraint that the longer time constant should be common across all samples. Using this constrained global fitting procedure, we found that the time constant for photoinjected electrons in GaAs was 5.5 ± 0.1 ns. The time constant associated with trapping of photogenerated electrons at the surface varied between the samples with different surface treatments and the values are displayed in Table I. The Si_3N_4 SP GaAs sample showed the longest surface trapping time with a time constant τ of 167 ± 1 ps, significantly longer than the time constant of the untreated GaAs sample (104 ± 1 ps). The increased trapping time indicates a successful reduction of the density of electron trapping states at the surface.

The surface-passivated sample without the Si_3N_4 encapsulation degraded in the weeks following passivation (the other samples were stable). This degradation is associated with a reduction in the surface trapping time constant and was thus easily observed. Three hundred and eleven days after the SP procedure, the surface-trapping time had stabilized to a value of 116 ± 1 ps. This value is significantly shorter than that of the encapsulated sample and is close to that of untreated GaAs (104 ± 1 ps).

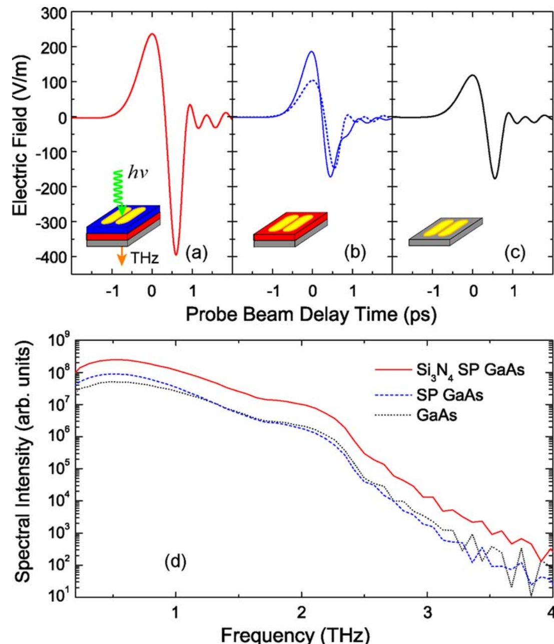

Fig. 3. (a)–(c) Emitted THz radiation from the PCS emitters from Si_3N_4 SP GaAs, SP GaAs, and GaAs, respectively. The insets of (a)–(c) show the geometries of the samples as in Fig. 1 with (yellow) electrode pads. The inset of (a) depicts the experimental geometry with the wavy (green) representing the incident IR radiation at 800 nm and the straight (orange) arrow as the produced THz radiation. The dotted curve in (b) are data taken approximately 117 days after fabrication (see text). The solid curve in (b) are the data for an SP GaAs sample that was fabricated and measured on the same day; these data are Fourier-transformed and represented in (d).

Therefore, while $(NH_4)_2S$ is effective at passivating the surface of GaAs, and hence, reducing the density of trapping sites for electrons, its effectiveness degrades over a period of months after treatment. However, by encapsulating the treated surface with Si_3N_4, the passivation effect is retained in the long term. Thus, the passivation and encapsulation process shows great promise for use in device fabrication.

V. PCS CHARACTERIZATION

The THz radiation generated from the passivated and encapsulated PCSs was characterized with an average incident power of the laser beam of 160 mW. The detector crystal used was a 0.2 mm (1 1 0) ZnTe crystal on a 6 mm substrate of (1 0 0) ZnTe.

The emitted THz radiation pulses are shown in Fig. 3 for antennas fabricated on Si_3N_4 SP GaAs, SP GaAs, and untreated GaAs. Once again, the Si_3N_4 SP GaAs demonstrates the largest electric field amplitude (see Fig. 3), with a spectrally integrated power that is $4.1\times$ that of GaAs. This may be attributed to the enhanced photoconductivity of the passivated and encapsulated material (see Fig. 2).

In the far-field approximation, the THz radiation pulse emitted from a photoconductive antenna has an electric field given by [18]

$$\overrightarrow{E}_{\mathrm{THz}} \propto \frac{1}{1+\sqrt{\epsilon}} \frac{\partial \overrightarrow{J}}{\partial t} \quad (1)$$

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where the current density within a semiconductor under an applied field $\overrightarrow{E}$ is $\overrightarrow{J} = \sigma\overrightarrow{E} + \overrightarrow{J_{\rm d}}$. The contribution of the diffusion current density $\overrightarrow{J_{\rm d}}$ can be neglected on the timescales of THz emission ($\sim$1 ps). Further postulating that $\epsilon \neq \epsilon(t)$ one finds that $E_{\rm THz}(t) \propto \partial J/\partial t = \partial(\sigma E)/\partial t$. The applied field E between the contacts of a PCS is rapidly screened by the formation of the radiating dipole, an effect, which can be modeled quantitatively by Monte Carlo simulations incorporating the 3-D solution of Poisson's equation [19]. Neglecting field-screening effects results in the prediction that $E_{\rm THz}(t) \propto E\partial\sigma/\partial t \propto \Delta\sigma/\Delta t$ if the photoconductivity rises within a certain time Δt.

The peak photoconductivity as measured in the OPTP experiments for the encapsulated and passivated sample was $1.4\times$ greater than that of the pristine reference sample (see Fig. 2); however, the observed emission strength was $2.2\times$ higher. This discrepancy may be a result of the photoconductivity rise time Δt altering on a faster timescale than our experimental resolution for OPTP. Such effects can be examined with time-domain spectroscopy in the mid-IR, which also allows $\epsilon(t)$ on subpicosecond timescales to be investigated [20].

The necessity of the encapsulation layer in protecting the passivated GaAs can be seen in Fig. 3(b). There, the emitted THz pulse from a pristine SP GaAs emitter (made from a pristine GaAs emitter by passivating in 20% $(NH_4)_2S$ for 10 min) is compared with that of a 117-day-old SP GaAs PCS. The new SP GaAs emitter has an electric field amplitude $1.8\times$ that of the old SP GaAs emitter. The encapsulated SP GaAs PCS has a peak $E_{\rm THz}$ [see Fig. 3(a)] that is $1.36\times$ larger than the new SP PCS, because of the reduced reflectivity of the Si_3N_4-coated material.

VI. Conclusion

We have investigated the influence of SP and encapsulation on the performance of THz emitters based on SI GaAs. An Si_3N_4 overcoating layer on surface-passivated GaAs was found to enhance the conductivity of the material, and to prevent oxidation of the PCS surface that would otherwise degrade performance over a timescale of many days. Possible further work includes assessing whether passivation enhances the conductivity of low-temperature grown or ion-implanted GaAs, such as commonly used in photoconductive detectors of THz radiation.

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Carl Headley is currently working toward the D.Phil. degree in physics at the University of Oxford, Oxford, U.K.

Lan Fu (SM'07) received the M.S. degree from the University of Science and Technology of China, Hefei, China, in 1996, and the Ph.D. degree from the Australian National University, Canberra, A.C.T., Australia, in 2001.

She was engaged in quantum-well intermixing in III–V materials and devices. She is currently a Fellow in the Department of Electronic Materials Engineering, Research School of Physics and Engineering, Australian National University. Her research interests include metal–organic chemical vapor deposition (MOCVD) growth of III–V semiconductor materials, design, fabrication, and integration of optoelectronic devices (lasers, IR photodetectors, and solar cells).

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Patrick Parkinson was born in Nottingham, U.K., in 1983. He received the M.Phys. degree in physics and the D.Phil. degree from the University of Oxford, Oxford, U.K., in 2005 and 2008, respectively.

He is currently a Postdoctoral Fellow in the Research School of Physics and Engineering, Australian National University, Canberra, A.C.T., Australia, where he is engaged in spectroscopic investigation of metal–organic chemical vapor deposition (MOCVD) grown III–V semiconducting nanowires. He was engaged in spectroscopic investigation of ultrafast electronic processes in nanoscale organic and inorganic semiconductors. From October 2008 to December 2009, he was a Postdoctoral Researcher in the Department of Physics, University of Oxford, where he was involved in terahertz spectroscopy of nanoscale semiconductors.

Xinlong Xu received the Ph.D. degree from the Institute of Physics, Chinese Academy of Sciences, Beijing, China, in 2006.

In 2007, he joined the Department of Physics at the University of Oxford, Oxford, U.K., as a Postdoctoral Research Assistant, where he has conducted research on femtosecond optical probe of mesoscopic materials for photovoltaics. His current research interests include terahertz technology and ultrafast pump–probe technology.

James Lloyd-Hughes received the D.Phil. degree from the University of Oxford, Oxford, U.K., in 2006.

For one year, he was a Postdoctoral Researcher at the University of Oxford, where he is currently a Career Acceleration Fellow (funded by the Engineering and Physical Sciences Research Council, U.K.) and a Lecturer in Physics at Brasenose College. From 2007 to 2009, he was at ETH Zurich, Switzerland, where he completed a Marie-Curie Fellowship funded by the European Union.

Chennupati Jagadish (F'02) was born and educated in India and worked in India and Canada prior to moving to Australia. He received the Ph.D. degree in physics from the University of Delhi, Delhi, India, in 1986.

He moved to Australia in 1990 and established a major research program in the field of semiconductor optoelectronics and nanotechnology at the Australian National University, Australian National University, Canberra, A.C.T., Australia. He has authored or coauthored more than 600 research papers (400 journal papers), hold five U.S. patents, coauthored a book, coedited a book, and edited 11 conference proceedings. He is an Editor of the *Progress in Quantum Electronics* and the *Journal of Semiconductor Technology and Science*. He is a member of the editorial board of 12 other journals.

Prof. Jagadish is an Associate Editor of the IEEE ELECTRON DEVICE LETTERS. He was elected as a Fellow of 13 professional societies/academies and received many awards and prizes.

Michael B. Johnston received the B.Sc. (Hons.) and the Ph.D. degrees from the University of New South Wales, Sydney, N.S.W., Australia, in 1996 and 2000, respectively.

He was a Postdoctoral Research Associate at the Cavendish Laboratory, University of Cambridge, from 1999 until 2002, where he undertook a joint program of research between the University of Cambridge and Toshiba Research Europe Limited. There he was engaged in developing a simulation to help explain the mechanisms of generating terahertz (THz) radiation in semiconductors. In 2002, he was appointed as a University Lecturer in the Department of Physics, University of Oxford, Oxford, U.K. He is a Fellow of Corpus Christi College, Oxford. His current research interests include THz spectroscopy of semiconducting nanostructures and polymers.

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