

PROCEEDINGS OF SPIE

SPIDigitalLibrary.org/conference-proceedings-of-spie

Terahertz emission from 2D nanomaterials

Kateryna Kushnir, Mengjing Wang, Ying Qin, Guangjiang Li, Sefaattin Tongay, et al.

Kateryna Kushnir, Mengjing Wang, Ying Qin, Guangjiang Li, Sefaattin Tongay, Kristie J. Koski, Lyubov V. Titova, "Terahertz emission from 2D nanomaterials," Proc. SPIE 10756, Terahertz Emitters, Receivers, and Applications IX, 107560S (14 September 2018); doi: 10.1117/12.2322160

SPIE.

Event: SPIE Optical Engineering + Applications, 2018, San Diego, California, United States

Terahertz emission from 2D nanomaterials

Kateryna Kushnir^a, Mengjing Wang^b, Ying Qin^c, Guangjiang Li^a, Sefaattin Tongay^c, Kristie J. Koski^d and Lyubov V. Titova^{*a}

^aDepartment of Physics, Worcester Polytechnic Institute, Worcester, Massachusetts 01609;

^bDepartment of Chemistry, Brown University, Providence, Rhode Island 02906, USA; ^cSchool for Engineering of Matter, Transport and Energy, Arizona State University, Tampa, AZ 85287, USA;

^dDepartment of Chemistry, University of California Davis, Davis, California 95616, USA

ABSTRACT

Group-IV monochalcogenides belong to a family of 2D layered materials. Monolayers of group-IV monochalcogenides GeS, GeSe, SnS and SnSe have been theoretically predicted to exhibit a large shift current owing to a spontaneous electric polarization at room temperature. Using THz emission spectroscopy, we find that above band gap photoexcitation with ultrashort laser pulses results in emission of nearly single-cycle THz pulses due to a surface shift current in multi-layer, sub- μm to few- μm thick GeS and GeSe, as inversion symmetry breaking at the crystal surface enables THz emission by the shift current. Experimental demonstration of THz emission by the surface shift current puts this layered group-IV monochalcogenides forward as a candidate for next generation shift current photovoltaics, nonlinear photonic devices and THz sources.

Keywords: Terahertz emission spectroscopy, terahertz generation, shift current, GeSe, GeS, 2D materials

1. INTRODUCTION

In 2D layered materials, atomic layers with strong in-plane covalent bonds stack together via weak van der Waals forces. The 2D material family that has recently attracted renewed attention is group-IV monochalcogenides GeS, GeSe, SnS and SnSe. They are non-toxic and composed of earth-abundant elements. With high optical absorption in the visible and near-infrared range, combined with predicted ultrahigh carrier mobility within the layers, they are promising for applications in solar energy conversion and optoelectronics. Recent theoretical predictions also suggest that group-IV monochalcogenide monolayers combine robust room temperature ferroelectricity and ferroelasticity with giant spontaneous electric polarization.¹⁻⁵ In-plane electric polarization results from an elastic distortion of the lattice, as the top and the bottom atoms shift in the armchair direction, as shown in Fig. 1(a)^{2,6}. Of group-IV monochalcogenides, GeS and GeSe are predicted to exhibit the highest polarization, $\sim 5 \times 10^{-10}$ C/m and $\sim 3 \times 10^{-10}$ C/m at zero temperature, respectively.² In-plane polarization breaks inversion symmetry of the monolayer, and can enable second order nonlinear optical effects such as optical rectification, a non-resonant effect, and a shift current, a resonant effect that is expected to dominate under above the band gap photoexcitation conditions.^{4,6,7} A shift current is an instantaneous spatial shift of electron density distribution along S-Ge or Se-Ge bond (Fig. 1 (a)).^{6,8} and it has been proposed as a mechanism behind the bulk photovoltaic effect (BPVE), a bias-free photocurrent generation that has been proposed as a mechanism for efficient third generation photovoltaics (Butler, Frost et al. 2015, Tan, Zheng et al. 2016). Here, we have used terahertz (THz) emission spectroscopy to explore generation of THz radiation in multi-layer GeS and GeSe crystals in response to the above band gap excitation with ultrashort laser pulses. We attribute the observed THz generation to the surface shift current in these 2D materials.

*ltitova@wpi.edu

2. EXPERIMENT

2.1 Sample fabrication

We have studied ultrafast photoinduced carrier dynamics in two systems: an array of GeS nanosheets of 10-30 μm length and $<1 \mu\text{m}$ width, and a GeSe crystal of $\sim 2 \text{ mm}$ in lateral dimensions. In both cases, 2D structures contained many layers, with thickness from $<1 \mu\text{m}$ (GeS) to few μm (GeSe). GeS nanosheets for this study were synthesized on sapphire substrates through the vapor-liquid-solid method using established procedures⁹. GeSe crystal with lateral dimensions of $\sim 2 \text{ mm}$ was grown using vapor transport, and thinned to sub- μm thickness by mechanical exfoliation using adhesive tape.

THz emission spectroscopy

THz emission spectroscopy allows electrical contact-free, all-optical monitoring of the photoexcited carrier dynamics by detecting, in the far field, THz radiation emitted by the sample.¹⁰⁻¹⁷ For the measurements, samples were excited at normal incidence with 400 nm, 100 fs laser pulses from a 1 kHz amplified Ti:Sapphire source, as illustrated schematically in Fig. 1(b). A pair of off-axis parabolic mirrors focused the emitted THz pulses onto a [110] ZnTe crystal where they were coherently detected by free-space electro-optic sampling.¹⁸ The wire-grid polarizer (Microtech Instruments; field extinction ratio of 0.01) ensured that only a vertically polarized component of the generated THz pulses was detected. Sample orientation was varied by rotation of a sample stage through an angle θ_{sample} , and the direction of the linear polarization of the optical pump pulse relative to the THz detection was varied by using a half-wave plate (not shown).

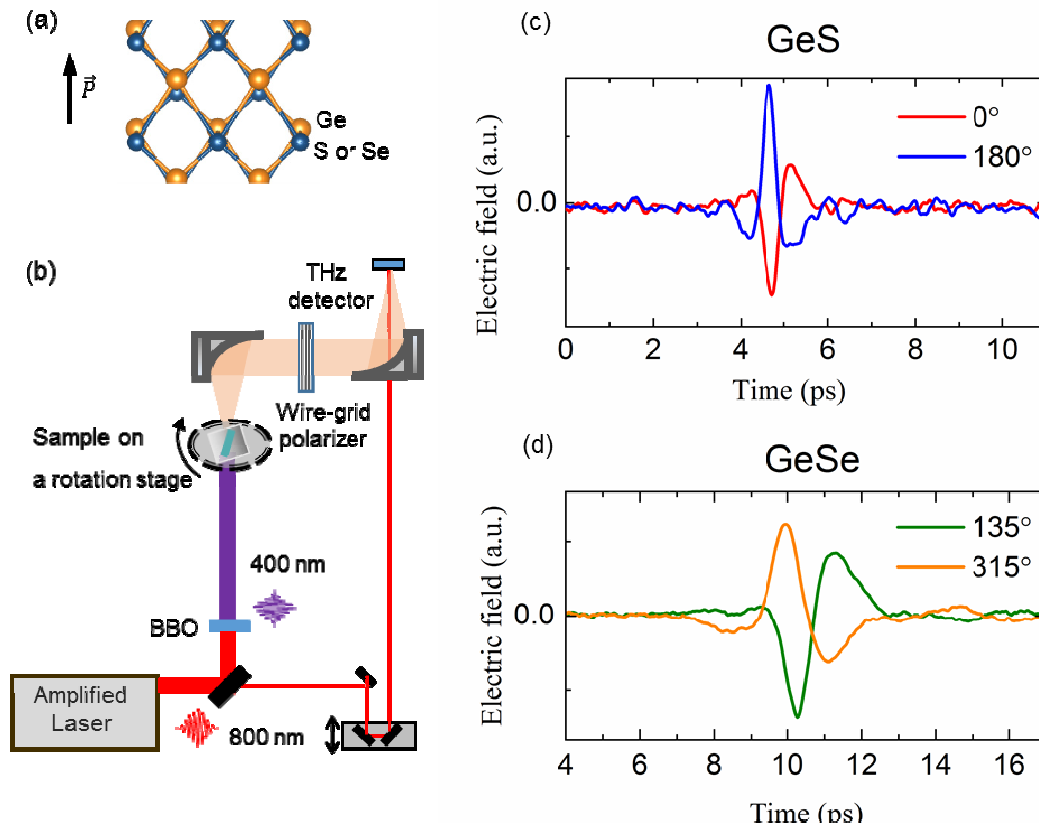


Figure 1. (a) A spontaneous electric polarization vector along the armchair direction in the surface layer of GeS or GeSe^{4,7}; THz waveforms taken at different sample orientations, indicating that rotating sample by 180° reverses polarity of the emitted pulse in (c) GeS ($15 \mu\text{J}/\text{cm}^2$ excitation fluence) and (d) GeSe ($190 \mu\text{J}/\text{cm}^2$ excitation fluence).

3. RESULTS AND DISCUSSION

Excitation with 400 nm (3.1 eV) pulses ensures direct interband excitation in both GeS and GeSe. We find that both systems emit nearly single-cycle electromagnetic field transients (Fig. 1 (c) and (d)). Normal incidence geometry, above band gap, linearly polarized excitation in the absence of external electrical bias suggest that the observed emission is indeed a result of a shift current.^{10, 19} Data shown in Figures 1(c) and 1(d) have been taken with the pump polarization unchanged and parallel to the THz detection. The figures shows that rotating the sample by 180° reverses the polarity of emission for both GeS and GeSe while the temporal shape of the waveform show only minimal change. This suggests the emission polarity is dictated by the symmetry breaking due to the intrinsic ferroelectric polarization, and supports the surface shift current as a mechanism of THz generation. Unlike the monolayers, bulk group-IV monochalcogenides do possess inversion symmetry, ruling out bulk shift current response. However, inversion symmetry is broken at the surface, indicating that the observed THz emission is due to a surface rather than bulk shift current. Shift current in response to photoexcitation suggests applications of these layered materials in BOVE photovoltaics and THz sources. Surface selectivity of THz emission in GeS and GeSe may also lead to new applications of these 2D materials in chemical sensing.

4. ACKNOWLEDGEMENT

We acknowledge support from the NSF DMR-1750944, and thank Benjamin Fregoso for insightful discussions.

REFERENCES

- [1] P.D. Antunez, J.J. Buckley, R.L. Brutchey, "Tin and germanium monochalcogenide IV-VI semiconductor nanocrystals for use in solar cells", *Nanoscale*, 3 2399-2411 (2011).
- [2] R. Fei, W. Kang, L. Yang, "Ferroelectricity and Phase Transitions in Monolayer Group-IV Monochalcogenides", *Phys. Rev. Lett.*, 117 097601 (2016).
- [3] L.C. Gomes, A. Carvalho, "Phosphorene analogues: Isoelectronic two-dimensional group-IV monochalcogenides with orthorhombic structure", *Physical Review B*, 92 085406 (2015).
- [4] S.R. Panday, B.M. Fregoso, "Strong second harmonic generation in two-dimensional ferroelectric IV-monochalcogenides", *Journal of Physics-Condensed Matter*, 29 (2017).
- [5] P. Zhao, H. Yang, J. Li, H. Jin, W. Wei, L. Yu, B. Huang, Y. Dai, "Design of new photovoltaic systems based on two-dimensional group-IV monochalcogenides for high performance solar cells", *Journal of Materials Chemistry A*, 5 24145-24152 (2017).
- [6] A.M. Cook, M.F. B, F. de Juan, S. Coh, J.E. Moore, "Design principles for shift current photovoltaics", *Nat Commun*, 8 14176 (2017).
- [7] T. Rangel, B.M. Fregoso, B.S. Mendoza, T. Morimoto, J.E. Moore, J.B. Neaton, "Large Bulk Photovoltaic Effect and Spontaneous Polarization of Single-Layer Monochalcogenides", *Phys. Rev. Lett.*, 119 067402 (2017).
- [8] M.H. Wu, X.C. Zeng, "Intrinsic Ferroelasticity and/or Multiferroicity in Two-Dimensional Phosphorene and Phosphorene Analogues", *Nano Lett.*, 16 3236-3241 (2016).
- [9] C. Li, L. Huang, G.P. Snigdha, Y. Yu, L. Cao, "Role of Boundary Layer Diffusion in Vapor Deposition Growth of Chalcogenide Nanosheets: The Case of GeS", *ACS Nano*, 6 8868-8877 (2012).
- [10] L. Braun, G. Mussler, A. Hruban, M. Konczykowski, T. Schumann, M. Wolf, M. Münzenberg, L. Perfetti, T. Kampfrath, "Ultrafast photocurrents at the surface of the three-dimensional topological insulator Bi₂Se₃", *Nature Communications*, 7 13259 (2016).
- [11] J.M. Schleicher, S.M. Harrel, C.A. Schmuttenmaer, "Effect of spin-polarized electrons on terahertz emission from photoexcited GaAs", *J. Appl. Phys.*, 105 113116 (2009).
- [12] M. Bieler, K. Pierz, U. Siegner, P. Dawson, "Shift currents from symmetry reduction and Coulomb effects in (110)-orientated GaAs/Al_{0.3}Ga_{0.7}As quantum wells", *Physical Review B*, 76 161304 (2007).
- [13] N. Laman, M. Bieler, H.M. van Driel, "Ultrafast shift and injection currents observed in wurtzite semiconductors via emitted terahertz radiation", *J. Appl. Phys.*, 98 103507 (2005).
- [14] S. Priyadarshi, M. Leidinger, K. Pierz, A.M. Racu, U. Siegner, M. Bieler, P. Dawson, "Terahertz spectroscopy of shift currents resulting from asymmetric (110)-oriented GaAs/AlGaAs quantum wells", *Appl. Phys. Lett.*, 95 151110 (2009).

- [15] K. Kushnir, M. Wang, P.D. Fitzgerald, K.J. Koski, L.V. Titova, "Ultrafast Zero-Bias Photocurrent in GeS Nanosheets: Promise for Photovoltaics", *ACS Energy Letters*, 1429-1434 (2017).
- [16] L.V. Titova, C.L. Pint, Q. Zhang, R.H. Hauge, J. Kono, F.A. Hegmann, "Generation of Terahertz Radiation by Optical Excitation of Aligned Carbon Nanotubes", *Nano Lett.*, 15 3267-3272 (2015).
- [17] F.R. Bagsican, X. Zhang, L. Ma, M. Wang, H. Murakami, R. Vajtai, P.M. Ajayan, J. Kono, M. Tonouchi, I. Kawayama, "Effect of Oxygen Adsorbates on Terahertz Emission Properties of Various Semiconductor Surfaces Covered with Graphene", *Journal of Infrared, Millimeter, and Terahertz Waves*, 37 1117-1123 (2016).
- [18] P.U. Jepsen, D.G. Cooke, M. Koch, "Terahertz spectroscopy and imaging—Modern techniques and applications", *Laser & Photonics Reviews*, 5 124-166 (2011).
- [19] F. Nastos, J.E. Sipe, "Optical rectification and shift currents in GaAs and GaP response: Below and above the band gap", *Physical Review B*, 74 035201 (2006).