

Engineering ultrafast carrier dynamics in GeS: nanostructuring and small molecule intercalation

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Abstract—Germanium sulfide (GeS) is a 2D semiconductor with high carrier mobility and a moderate band gap of about 1.5 eV, which holds promise for high-speed optoelectronics and photovoltaics. We use time-resolved THz spectroscopy to investigate ultrafast carrier dynamics in in GeS single crystals as well as in GeS nanoribbons. In both bulk and nanostructured GeS, we find that near gap excitation at 1.55 eV results in much longer lived photocarriers compared to 3.1 eV excitation. We also explore how intercalation of small molecules influences the photoexcited carrier dynamics in GeS. We find that presence of edge states in nanoribbons results in decreased carrier lifetime. Organic molecules such as octylamine, which do not form chemical bonds with the host GeS layers, increase photoexcited carrier lifetime. These findings demonstrate the possibility of engineering the properties of 2D materials by intercalation.

I. INTRODUCTION

GeS is a 2D van der Waals semiconductor with high carrier mobility and a moderate band gap (~1.5 eV in the bulk), which holds promise for high-speed optoelectronics and energy conversion.^{1, 2} Theory predicts that GeS monolayers are multiferroic, combining a robust ferroelasticity and ferroelectric polarization at room temperature.^{3, 4} We have previously demonstrated that room temperature ferroelectric polarization in GeS results in the THz emission due to an ultrafast photoexcited shift current in response to above the band gap excitation.² Here, we use time-resolved THz spectroscopy (TRTS), a noncontact probe of microscopic photoconductivity, to explore the photoexcited carrier dynamics in bulk and nanostructured GeS, and explore the possibility of tuning the electronic properties and photoexcited carrier dynamics in this material by intercalation of conjugated organic molecules.

The ability to insert foreign species – molecules, ions and atoms into (intercalate) or out (deintercalate) of the van der Waals gap,⁵⁻⁷ of layered 2D materials has the potential to change the doping level, charge carrier density, and mobility, as well as introduce new localized or extended energy states. These changes most readily manifest as changes in conductivity, optical absorption, as well as changes in the nature and dynamics of the photoexcitations

II. RESULTS AND DISCUSSION

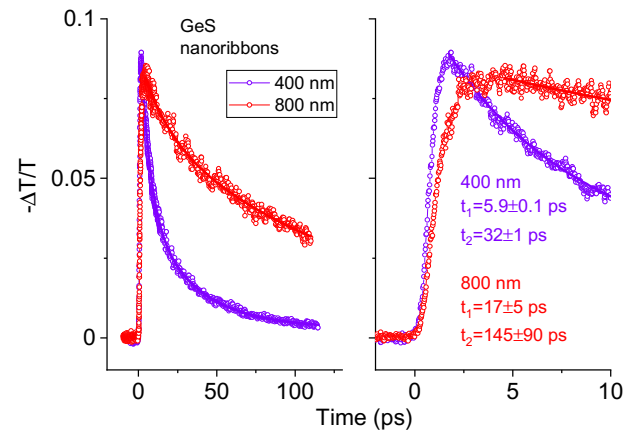


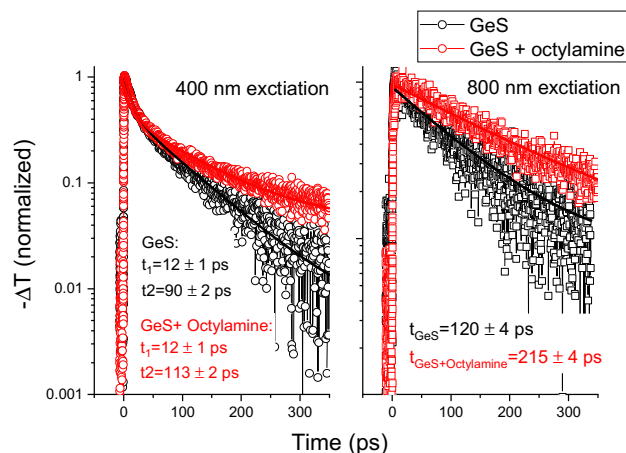
Fig. 1. (a) Transient THz photoconductivity excited in GeS nanoribbons with 400 nm or 800 nm pulses with average power of 30 mW. Right panel shows early time dynamics.

Fig. 1 shows transient THz photoconductivity in GeS nanoribbons. GeS nanoribbons with lateral dimensions on the order of 100-500 nm, lengths of few μm , and thickness ~ 50 -100 nm were grown on quartz substrate through vapor-liquid-solid method as described previously.² We find that excitation with 800 nm (1.55 eV) light with energy very close to the bulk band gap of GeS results in a long-lived photoconductivity that is also characterized by a slow, ~ 2 ps rise time. In our previous studies, 800 nm excitation did not result in an ultrafast surface shift current that results in THz emission. We hypothesize that 800 nm excitation access only the bulk states, and that the slow rise time occurs as a result of scattering of photoexcited carriers between three pairs of valleys observed in GeS band structure near the gap.⁸ Excitation with energy significantly exceeding the gap (400 nm, or 3.1 eV) has been earlier demonstrated to photoexcited ultrafast surface shift currents. It also results in the rapid onset of photoconductivity that decays over significantly shorter time scales (tens vs hundreds of picoseconds) as seen in Fig. 1. This drastic difference in carrier lifetimes in response to excitation with different photon energies opens exciting prospects for applications in wavelength-sensitive ultrafast photodetectors.

Fig. 2 shows transient photoconductivity in bulk, single crystalline GeS (black curves). First of all, both 400 nm and 800 nm excitation result in significantly slower decay of photoconductivity in a bulk crystal compared to the ribbons due to the absence of the edge states that can efficiently trap charge

carriers.

Also in Fig. 2, we show the transient photoconductivity in GeS single crystal intercalated with octylamine through chemical reflux. *Ab initio* calculations of the intercalation energies and the charge transition levels *show that* intercalants such as of octylamine, form no chemical bonding with the host 2D GeS and behave as pseudo-alkali metals, transferring electrons. We find that octylamine intercalation increases the lifetime of photoexcited carriers.



We are also exploring intercalation with thiophene and pyridine as well as with zero-valent copper. *Ab initio* modeling, structural characterization, and time-resolved THz spectroscopy are used to investigate the mechanisms that underpin the influence of structure, morphology, and intercalation of organic molecules into the van der Waals gap and lay foundations for engineering GeS for advanced application.

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Fig. 2. (a) Transient THz photoconductivity in single crystalline GeS and in GeS intercalated with octylamine, excited with 400 nm (left) or 800 nm (right) pulses with average power of 30 mW.

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