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Ultrafast carrier dynamics in 2D GeS in response to photoexcitation across the visible-NIR range

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ABSTRACT

Germanium sulfide (GeS) is a 2D semiconductor with high carrier mobility, a moderate band gap of about 1.6 eV, and highly anisotropic optical properties. In-plane anisotropy and a large in-plane spontaneous electric polarization in GeS monolayers have been predicted to result in significant second order nonlinear effects in response to above-the-gap excitation with photon energy > 2.5 eV[1]. We have further confirmed it experimentally by demonstrating surface shift current generation in GeS using THz emission spectroscopy with 3.1 eV excitation.[3] Here, we use time-resolved THz spectroscopy to investigate the dynamics and lifetimes of photoexcited carriers in GeS single crystals and nanoribbons in response to excitations with energies ranging from 1.5 eV, resonant with the bulk gap, to 3.1 eV. We find that resulting dynamics vary considerably. Lower energy (1.5 eV) excitation injects carriers directly into three low-lying valleys in the conduction band. Those carriers have long, which photoconductivity persisting for over 500 ps, as it can be seen in Fig. 1(a). On the other hand, injecting carriers high into the conduction band results in THz emission due to the shift current as well as into transient photoconductivity that recovers over <100 ps. Pronounced changes in the transient photoconductivity in response to optical excitation with photon energy across the visible-NIR range open intriguing possibilities for applications in ultrafast spectrally-sensitive photodetectors and solar energy conversion.

Keywords: Germanium Sulfide, 2D layered Materials, Semiconductors, THz Spectroscopy, Photoconductivity, Anisotropy, Optical properties

1. INTRODUCTION

GeS is a 2D layered semiconductor with high carrier mobility, a moderate band gap (~1.6 eV in the bulk), and predicted significant second order nonlinear effects in response to above-the-gap excitation with photon energy, making it attractive for high-speed optoelectronics, field effect transistors, and energy conversion.[2, 3] Studies predict that GeS monolayers have anisotropic in-plane crystal structures are multiferroic, combining a robust ferroelasticity and ferroelectric polarization at room temperature and.[4, 5, 6] In our recent work we have demonstrated that in-plane anisotropy in GeS results in the THz emission due to an ultrafast photoexcited shift current in response to above the band gap excitation.[3] In this work, we use time-resolved THz spectroscopy (TRTS), a noncontact probe of microscopic photoconductivity, to investigate the dynamics and lifetimes of photoexcited carriers in nanostructured GeS.

2. RESULTS AND DISCUSSION

2.1 Dependence of photoexcited carrier dynamics on excitation energy

Flat GeS nanoribbons and sheets with lateral dimensions on the order of 200-500 nm, 20-40 μm lengths, thickness ~ 50-100 nm, and were synthesized through vapor-liquid-solid (VLS) method on quartz substrate as descried in [3]. We investigated transient THz photoconductivity following photoexcitation with either 800 nm (1.55 eV) light, with energy just below the bulk band gap of GeS, or 400nm (3.1 eV), with energy significantly exceeding the bandgap. We found that resulting dynamics of photoexcited carriers vary considerably. Transient THz photoconductivity in GeS nanoribbons is shown in Figure 1. We find that both 800nm and 400nm excitation result in transient photoconductivity in GeS.

We observe that the excitation with 800 nm results in a slower onset and a significantly longer recovery compared to 400 nm. We hypothesize that lower energy (1.5 eV) excitation injects carriers directly into three lowest valleys in the conduction band of GeS. In this case, the slow rise time (Fig. 1(b), ~ 1 ps) occurs as a result of inter-valley scattering of photoexcited carriers between from lower to higher mobility valleys in GeS band structure near the bandgap.[7] In

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agreement with our previous work, we did not observe shift current emission for 800nm excitation. However, injecting carriers high into the conduction band with energy much higher than the bandgap energy results in THz emission due to the shift current as well as into rapid rise of transient photoconductivity (~ 0.5 ps, Fig. 1(b)) with a much shorter-lived photoconducitivy which decays over tens of picoseconds vs hundreds of picoseconds for 800 nm excitation (Fig. 1(a)). In both case, we find that the decay of photoconductivity is bi-exponential, indicative of different relaxation mechanisms such as trapping at defects and edge states. The decay parameters for both 800 nm and 400 nm are reported in the Fig. 1(a) legend. Observed differences suggest that the carriers excited higher into CB/VB by 400 nm pulses do not relax down to the lowest states accessible with 800 nm excitation and are more susceptible to trapping in defect/edge states, resulting in shorter lifetimes. This demonstrates that carriers excited by different energies access different states in GeS band structure which exhibit different properties across the visible-NIR range,suggesting promising prospects for applications in ultrafast wavelength-sensitive photodetectors and solar energy conversion.

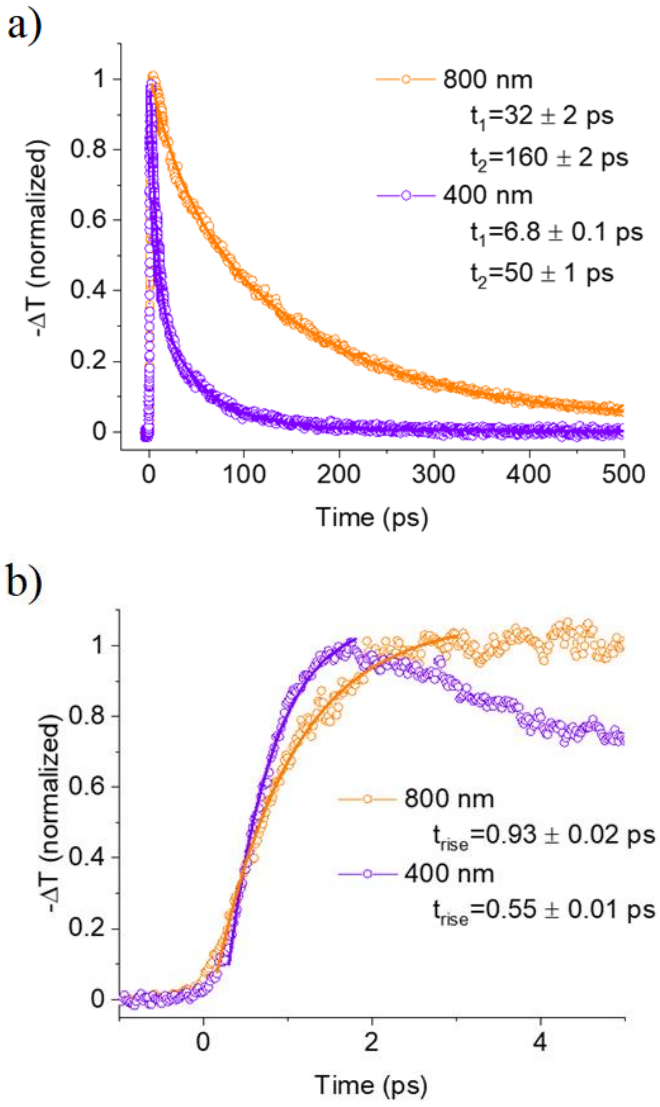

Fig. 1 Transient THz photoconductivity excited in GeS nanoribbons with 400 nm or 800 nm pulses with average fluency of 300 μJ/cm^2. a) Decay and b) rise time of charge carriers dynamics

2.2 Excitation Fluence Dependency

Fig. 2 shows transient photoconductivity in GeS nanoribbons for different excitation fluence values First,we note that the peak of photoconductivity is ~ a factor of 2 higher for 800nm excitation compared to 400 nm excitation, despite a lower absorbance. In addition,, we find that increase in the fluence of excitation does not impact the rise time of photoconductivity, but slows its decay for 400 nm excitation. Increase in photoinduced carrier lifetime following excitation with higher fluence values of 400 nm maybe indicative of saturation of trap states. On the other hand, the dynamics of photoconductivity following 800 nm excitation is not affected by injecting more carriers, providing another piece of evidence that the carriers injected directly into the low-lying valleys are not as susceptible to trapping. Future work comparing the transient conductivity in the single crystalline bulk GeS to that in the nanoribbons will shed more light onto the mechanisms at play.

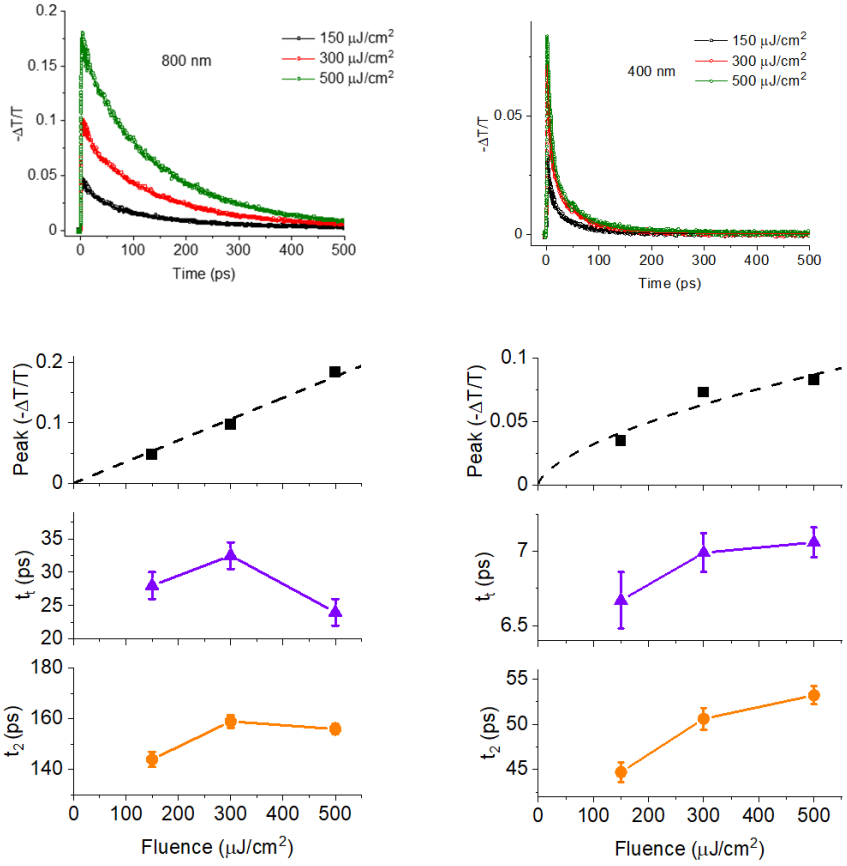

Fig. 2. Excitation fluence dependency of photoexcited carrier dynamics at 800nm (left) and 400nm (right) pulses.

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