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Tailoring ultrafast carrier dynamics in GeS and GeSe via Cu intercalation

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***Abstract*—Germanium sulfide (GeS) and germanium selenide (GeSe) are layered 2D van der Waals materials that belong to a family of group-IV monochalcogenides. These semiconductors have high carrier mobilities and moderate band gaps in the near infrared. Additionally, we have demonstrated that above gap photoexcitation results in ultrafast surface photocurrents and emission of THz pulses due to a spontaneous ferroelectric polarization that breaks inversion symmetry in the monolayer. Beyond the sub-picosecond time scales of shift currents, photoexcited carriers in both materials result in long-lived transient conductivity. We find that 800 nm excitation results in longer lived free photocarriers, persisting for hundreds of picoseconds to several nanoseconds, compared to tens to hundreds of picoseconds lifetimes for 400 nm excitation. Here, we report on tailoring the free photoexcited carrier lifetimes by intercalation of zero-valent Cu into the van der Waals gaps of GeS and GeSe. Density functional theory calculations predict that Cu atoms introduce mid-gap states. We demonstrate that intercalating only ~ 3 atomic % of zero-valent Cu reduces the carrier lifetime by as much as two-to-four-fold, raising the prospects of these materials being used for high-speed optoelectronics.**

I. Introduction

GeS and GeSe are 2D van der Waals materials with orthorhombic crystal structure belonging to the Pnma space group and multilayer band gaps in the near-infrared infrared (1.55-1.65 eV for GeS and 1.1 eV for GeSe).[1-4] High carrier mobility and a moderate band gap make them promising materials for high-speed optoelectronics and energy conversion.[5-7] Broken inversion symmetry associated with a spontaneous ferroelectric polarization in the monolayers and surface layers results in anisotropic electronic and optical properties.[8, 9] We have recently demonstrated that above-gap photoexcitation of both GeS and GeSe with 100 fs short laser pulses results in zero-bias in-plane shift current and emission of THz pulses, bringing forth possible applications as THz source materials.[10, 11]

Here, we focus on investigating the photoexcited carrier dynamics in GeS and GeSe beyond the initial sub-picosecond response that yields THz emission, using Cu intercalation to tailor the photoexcited carrier lifetimes. Intercalation and deintercalation, the ability to insert foreign species (molecules, ions and atoms) into or out of the van der Waals gap of layered 2D materials, can introduce new energy states and change charge carrier density and mobility, which leads to the modification of conductivity and optical absorption.[12-14]

We investigate the effects of the intercalation on transient conductivity of GeS and GeSe using time-resolved THz spectroscopy (TRTS), a noncontact probe of microscopic photoconductivity. First-principles self-consistent quasiparticle Green's function and screen Coulomb interactions (scqGW) within the VASP electronic structure code[15] are used to model the effects of Cu intercalation on the optoelectronic properties of GeSe bilayers.

II. Results and Discussion

We find that in both GeS and GeSe, photoexcitation by either 800 nm or 400 nm pulses results in long-lived transient conductivity with photoexcited carrier lifetimes that are determined by the sample morphology viz. single crystalline vs nanoribbons and by the excitation photon energy. In bulk and nanostructured GeS and GeSe, 1.55 eV (800 nm) excitation results in much longer lived free photocarriers, persisting for hundreds of picoseconds in nanoribbons and several nanoseconds in single crystals, as compared to tens to hundreds of picoseconds lifetimes for carriers excited with 3.1 eV (400 nm) pulses.[16]

We also demonstrate tuning of the photoexcited carrier

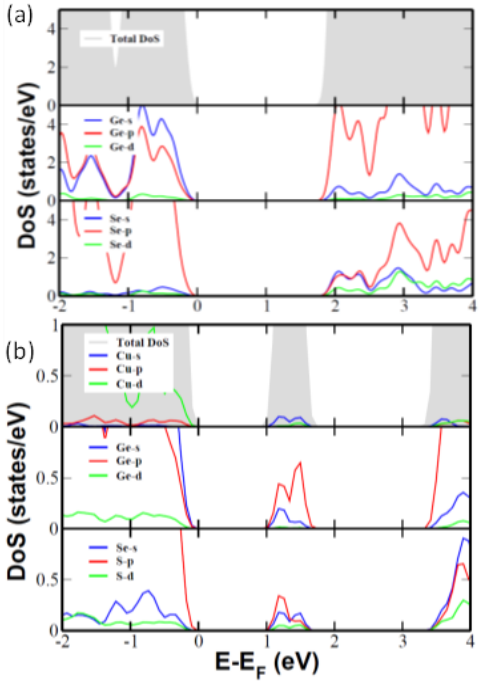

Fig. 1. Density of states for GeSe bilayer (a) and GeSe bilayer intercalated with Cu (b) obtained using advanced scqGW method.

lifetimes by intercalation of zero-valent Cu. Many-body effects are crucial for the proper description of the optoelectronic properties of 2D-based materials. The scqGW method is used to obtain the electronic properties of the pristine and Cu-intercalated structures characterized by the density of states (DoS). As illustrated in Fig. 1 (a), the quasiparticle band gap of GeSe bilayer is ~ 1.8 eV, which is larger than the ~ 1.1 eV gap for a multilayer. Cu intercalation into the van der Waals gap of GeSe at a concentration of approximately 3.03% results in the formation of intermediate band (IB) states (Fig. 1(b)).

The corrugated structure of GeS and GeSe hinders intercalation and limits the atomic percent of Cu to ~3%, [13] but we find that it is sufficient to introduce IB states that reduce the carrier lifetime by as much as two-to-four-fold.

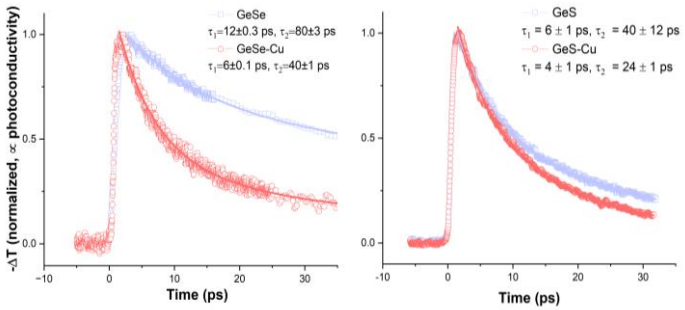

Fig. 2. Transient THz photoconductivity excited in GeS and GeSe nanoribbons with and without Cu intercalation with 400 nm pulses.

As illustrated in Fig.2, excitation of pure and Cu-intercalated GeS and GeSe nanoribbons with 400 nm, 100 fs pulses results in a fast onset of photoconductivity followed by its decay, represented by a transient change in the THz probe pulse peak. Pure GeSe photoconductivity dynamics exhibit biexponential decays with a fast component of ~12 ps and a longer-lived component of ~80 ps. Intercalation of Cu decreases the carrier lifetime by half, making the fast component ~ 6ps and longer-lived component ~40 ps. Similarly, in the case of pure GeS, photoconductivity dynamics exhibit biexponential decay with a fast component ~ 6 ps and longer-lived component of ~ 40 ps. Introduction of copper into GeS decreases the fast and long components almost two times. Intercalation similarly reduces the lifetime of long-lived carriers excited with 800 nm pulses. At the same time, Cu intercalation is not found to impact THz emission properties, as neither the intensity nor the bandwidth of THz emission in response to 400 nm excitation is affected.

In summary, intermediate band states introduced by Cu in GeS and GeSe are shown to behave as traps for photoexcited carriers, resulting in a significant decrease of carrier lifetime for both GeS and GeSe while not impacting THz emission properties. Understanding the effects of zero-valent metal intercalation will lay the foundations for advanced engineering of 2D group-IV monochalcogenides for applications in THz and optical photonic devices.

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