Engineering Ultrafast Photoconductive Response in SnS_2 Through Metal Intercalation

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ABSTRACT

SnS_2 is a two-dimensional (2D) layered semiconductor with a visible-range bandgap (~2.3 eV), high charge carrier mobility, long carrier lifetimes, and good environmental stability. This study explores the impact of zero-valent metal intercalation into the van der Waals gaps of SnS_2 on charge carrier dynamics. We demonstrate that metal intercalation enhances optical absorption in the yellow-to-IR range and induces metal-dependent bandgap shifts. Time-resolved THz spectroscopy reveals that different metals uniquely influence photoconductivity dynamics: We find that intercalation with Bi, Ni, and Fe shortens the photoconductivity decay times, whereas Rh intercalation results in a slower decay. These findings highlight the potential of metal intercalation to tailor SnS_2 properties for diverse applications, from solar energy conversion to high-speed photodetectors.

Keywords: Intercalation, SnS_2, THz spectroscopy, Carriers dynamics, Ultrafast dynamics, 2D materials

1. INTRODUCTION

SnS_2 is a two-dimensional (2D) layered semiconductor with a visible-range bandgap (~2.3 eV) and excellent environmental stability.[1] Previously, we investigated transient photoconductivity dynamics in SnS_2 under above-bandgap (400 nm) excitation, finding that photoexcited free carriers exhibit high mobility of 250 ± 10 cm² V^{-1} s^{-1} and lifetimes in the hundreds of picoseconds.[2] In this study, we examine the effects of zero-valent metal intercalation on the charge carrier dynamics of SnS_2. Zero-valent intercalation involves introducing atomic metals into the van der Waals gap of 2D materials without significantly altering the structure or oxidation state of the host lattice. [3-5] This technique has been shown to enhance mobility and reduce carrier lifetimes in GeS under near-gap excitation.[6] Here, we employ time-resolved THz spectroscopy (TRTS)—a non-contact method for probing microscopic photoconductivity—to investigate the dynamics and lifetimes of photoexcited carriers in SnS_2 following both above-gap (400 nm) and sub-gap (800 nm) excitation.

2. RESULTS AND DISCUSSION

Single-crystalline SnS_2 (few microns thick, 1–10 mm crystals) was synthesized via chemical vapor transport at ~650°C using I_2 as the transport agent, following previously described methods. [2, 7] X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) confirmed the phase purity of the resulting SnS_2 crystals. Zero-valent metal atoms were intercalated into the van der Waals gaps between the layers using a wet-chemical process, for the concentration of intercalated atoms < 3 atm.%.[8]

Optical Absorbance

We first examined the impact of intercalation on optical absorbance in the ultraviolet–near-infrared (UV-NIR) range. **Figure 1** presents the normalized UV-NIR absorption spectra for pristine SnS_2 and the four intercalated SnS_2 samples. The spectra reveal a redshift in the bandgaps of Bi-,Rh-, Cu-, and Ni-intercalated SnS_2, ranging from 6 to 25 nm, as

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indicated in the legends of the respective panels. Additionally, all intercalated samples exhibit enhanced optical absorption in the yellow-IR range. We attribute this to the emergence of mid-gap states, a phenomenon previously observed in Cu-intercalated MoS_2[5] and GeS[6].

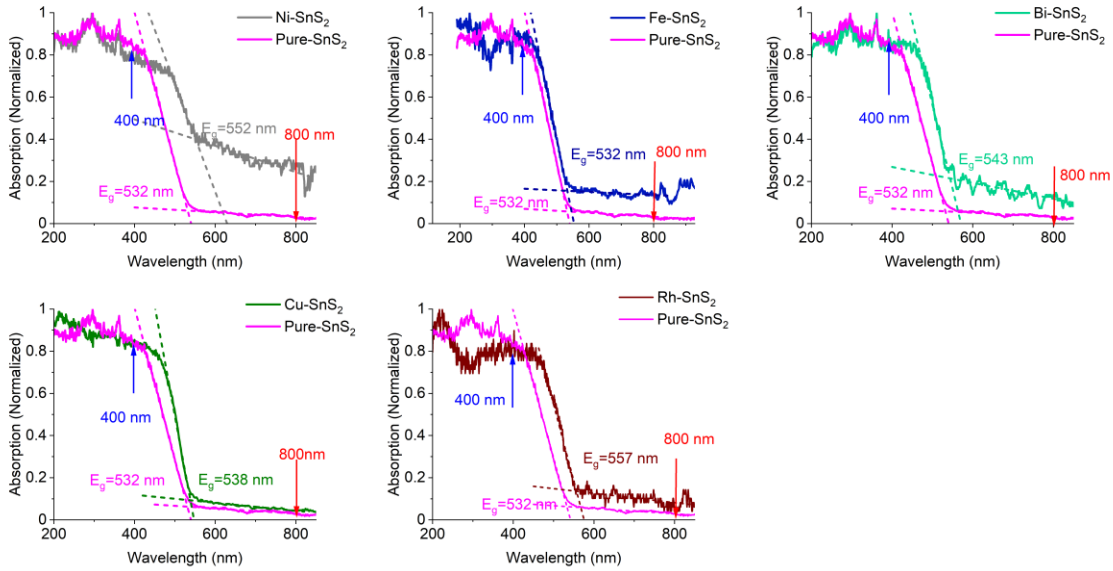

Figure 1. Optical absorbance in the UV-NIR range for pristine SnS_2 compared with intercalated SnS_2. Panels show spectra for: (a) Bi-SnS2, (b) Cu-SnS_2, (c) Ni-SnS_2, and (d) Fe-SnS_2.

Time-resolved THz photoconductivity

we conducted time-resolved terahertz (TRTS) spectroscopy measurements to investigate the dynamics and lifetimes of photoexcited carriers in both pristine and intercalated SnS_2 samples. TRTS is a pump-probe technique in which changes in the transmission of a THz probe pulse are measured as a function of delay time. The negative changes in transmission of the THz probe pulse peak are proportional to the transient photoconductivity, as expressed by the relation $-\frac{\Delta T\,(t)}{T} \propto \Delta\sigma\,(t)$.[6] We studied transient THz photoconductivity following photoexcitation with either 800 nm (1.55 eV) light, which has energy below the band gap of SnS_2, or 400 nm (3.1 eV) light, which has energy above the band gap of SnS_2.

Pristine SnS_2	$\mathbf{t_1 = 6 \pm 0.1\ ps}$	$\mathbf{t_2 = 38 \pm 1\ ps}$	$\mathbf{t_3 = 215 \pm 3\ ps}$
Rh-SnS_2	$t_1 = 7 \pm 0.2$ ps	$t_2 = 45 \pm 2$ ps	$t_3 = 256 \pm 5$ ps
Cu-SnS_2	$t_1 = 3.5 \pm 0.1$ ps	$t_2 = 25 \pm 2$ ps	$t_3 = 221 \pm 2$ ps
Ni-SnS_2	$t_1 = 7 \pm 0.3$ ps	$t_2 = 36 \pm 3$ ps	$t_3 = 151 \pm 5$ps
Fe-SnS_2	$t_1 = 4.6 \pm 0.3$ ps	$t_2 = 29 \pm 2$ ps	$t_3 = 138 \pm 4$ ps
Bi-SnS_2	$t_1 = 3.6 \pm 0.1$ ps	$t_2 = 22 \pm 0.4$ ps	$t_3 = 142 \pm 1$ ps

Table 1. The tri-exponential photoconductivity decay times, t_1, t_2, and t_3, measured for pristine SnS_2 and SnS_2 intercalated with Cu, Bi, Ni, Fe, and Rh, following photoexcitation with a 400 nm laser pulse at a fluence of 170μJ/cm^2.

With 400 nm excitation, we observed that the dynamics of photoexcited carriers change upon intercalation. Figure 2 shows the photoconductivity dynamics for pristine SnS_2 and SnS_2 intercalated with Fe, Bi, Ni, Rh, and Cu metal atoms. In our previous studies, we demonstrated that above-bandgap excitation in SnS_2 induces a shift current and breaks inversion symmetry due to stacking faults, which leads to THz emission.[2] In the following sections, transient THz photoconductivity decays are presented after subtracting the THz emission contributions from all the samples. The photoconductivity decay follows a tri-exponential behavior, yielding time constants t_1, t_2, and t_3, which suggest multiple recombination and trapping mechanisms involving defects, mid-gap states, and other contributors to the relaxation process. We observe that

intercalation with Bi, Ni, and Fe shortens the photoconductivity decay times, whereas Rh intercalation results in a slower decay. In the case of Cu intercalation, the initial decay is faster, but the later stages of decay exhibit a slower rate, as shown in Table 1.

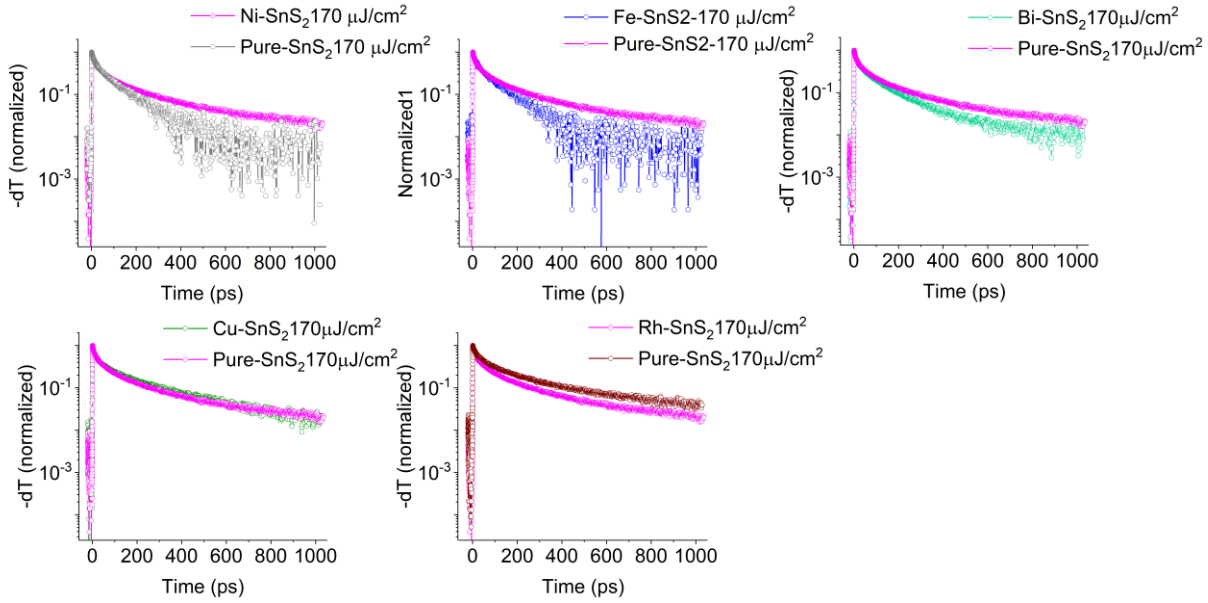

Figure 2. Transient THz photoconductivity excited in pristine SnS_2 and Fe, Bi, Cu, Rh, and Ni intercalated SnS_2 with 400 nm pulses. The legends indicate the sample names and photoexcitation fluence. The tri-exponential photoconductivity decay times are provided in Table 1.

Finally, we demonstrate that the samples can also be photoexcited with energies below the bandgap. However, as shown in Fig. 3, photoconductivity at 800 nm is significantly weaker compared to excitation above the bandgap. Fig. 3 illustrates the transient THz photoconductivity response for both 800 nm (below-bandgap) and 400 nm (above-bandgap) excitations. We find that 400 nm excitation, which injects carriers deep into the conduction bands, results in a rapid rise of transient photoconductivity (approximately three times faster) and much shorter-lived photoconductivity, decaying over tens of picoseconds, compared to the hundreds of picoseconds (>500 ps) observed with 800 nm excitation in all the samples. In the case of Ni, 800 nm excitation leads to a suppression of photoconductivity, reflecting the metallic behavior of Ni-intercalated SnS_2. We hypothesize that Ni intercalation introduces a significant concentration of free electrons. Below-gap photons are absorbed by these free carriers, increasing their kinetic energy and leading to rapid lattice heating via efficient carrier-phonon scattering. As typically seen in metals, the elevated lattice temperature results in higher electron-phonon scattering, reducing carrier mobility and conductivity. Future studies will investigate how the concentration of Ni influences these effects and aim to identify other intercalants that produce similar behavior. These findings suggest that intercalation can be a powerful tool for tuning carrier dynamics, with potential applications ranging from solar energy conversion—where longer carrier lifetimes are advantageous—to high-speed photodetectors, where faster response times are critical.

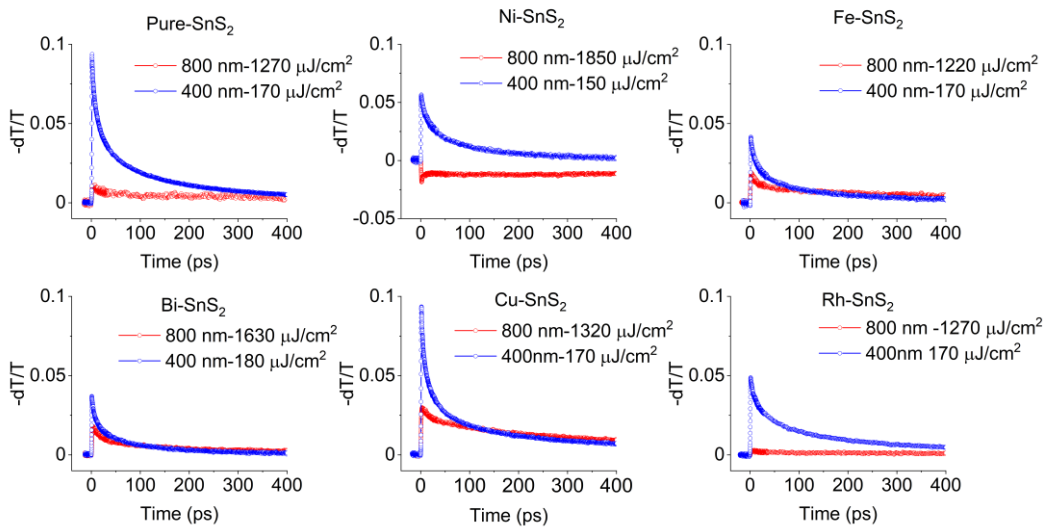

Figure 3. Transient THz photoconductivity excited in pristine SnS_2 and Fe, Bi, Cu, Rh, and Ni intercalated SnS_2 with 400 nm (above bandgap) vs 800 nm (below bandgap) pulses.

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