



# Ultrafast Nonlinear Optical Response and Carrier Dynamics in Layered Gallium Sulfide (GaS) Single-Crystalline Thin Films

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### Specialty section:

This article was submitted to  
Semiconducting Materials and  
Devices,  
a section of the journal  
Frontiers in Materials

Received: 14 September 2021

Accepted: 04 October 2021

Published: 22 October 2021

### Citation:

Lu H, Chen Y, Yang K, Kuang Y, Li Z  
and Liu Y (2021) Ultrafast Nonlinear  
Optical Response and Carrier  
Dynamics in Layered Gallium Sulfide  
(GaS) Single-Crystalline Thin Films.  
Front. Mater. 8:775048.  
doi: 10.3389/fmats.2021.775048

Gallium sulfide (GaS) is a layered metal monochalcogenide semiconductor that has recently garnered considerable attention in various fields. In this study, we investigated the nonlinear absorption characteristics of multilayer  $\beta$ -GaS thin films on sapphire substrate by using femtosecond open-aperture Z-scan method. The  $\beta$ -GaS films exhibit saturable absorption behavior at 532 nm while nonlinear absorption appears under 650 nm excitation. The nonlinear absorption coefficient of  $\beta$ -GaS was determined to be  $-1.8 \times 10^{-8}$  m/W and  $4.9 \times 10^{-8}$  m/W at 532 and 650 nm, respectively. The carrier dynamics of  $\beta$ -GaS films was studied via femtosecond transient absorption (TA) measurements. The TA results demonstrated that  $\beta$ -GaS films have broad photo-induced absorption in the visible regime and sub-nanosecond lifetime. Our results indicate that gallium sulfide has large nonlinear optical response and long carrier lifetime, which could be applied in future photonic devices.

**Keywords:** gallium sulfide, metal monochalcogenide, Z-scan technique, transient absorption spectroscopy, layered semiconductor

## INTRODUCTION

Two-dimensional (2D) semiconductors, such as transition metal dichalcogenides (TMDC) and black phosphorene (BP), have attracted significant research attention in the last decade due to their intriguing physical properties and prospects for technological applications in optoelectronics, sensors, nanoelectronics, etc (Mak and Shan, 2016; Akinwande et al., 2019; Liu et al., 2020). The electrical, optical and thermal properties of various 2D materials such as MoS<sub>2</sub>, WSe<sub>2</sub>, h-BN, Bi<sub>2</sub>Te<sub>3</sub> and SnSe have been widely studied (Briggs et al., 2019; Tan et al., 2020). Previous results demonstrate that the bandgap of 2D semiconductors is thickness- and size-dependent. And the weak van der Waals forces between adjacent layers in 2D semiconductors enable the formation of layered van der Waals heterojunctions, which is essential for transistor and detector applications (Liu et al., 2016). However, the stability upon exposure to air impedes the applications of 2D semiconductors in practical devices. Therefore, investigation of novel 2D materials with superior properties and stability is critical for future development of 2D semiconductor optoelectronic and photonic devices.

Group-III metal monochalcogenide MX (M = Ga and Ge, X is a chalcogen such as S and Se) is also a layered semiconductor with atomic-thick layers of metal and chalcogen atoms, which has received research interest in recent years (Cai et al., 2019; Yang and Hao, 2019). Compared to TMDC and BP, the photo-physical properties of metal monochalcogenides are still elusive. Gallium sulfide (GaS) is a

member of the group-III monochalcogenide semiconductors. Previous results show that bulk GaS has an indirect bandgap of 2.5 eV and direct bandgap of 3.0 eV (Ho and Lin, 2006; Jastrzebski et al., 2019). Recently, a number of research groups have investigated the electronic and optical response of GaS in both bulk and 2D forms. Their results show that GaS has fascinating properties that could be used in transistors, LEDs, photodetectors, catalysts, etc (Late et al., 2012; Hu et al., 2013; Harvey et al., 2015; Jung et al., 2015; Lu et al., 2020; Tverjanovich et al., 2020; Zappia et al., 2021). Despite these efforts, however, few reports are available in literature about the nonlinear optical (NLO) properties of GaS (Allakhverdiev et al., 1997; Kato and Umemura, 2011; Isik et al., 2013; Karatay, 2019; Deckoff-Jones et al., 2021; Xu et al., 2021). And previous results on NLO response of GaS were carried out with picosecond (ps), nanosecond (ns) and continuous wave (CW) laser (Isik et al., 2013; Karatay, 2019; Xu et al., 2021). The ultrafast NLO properties of GaS films are scarcely explored. On the other hand, a deeper understanding of the carrier dynamics in semiconductor material is extremely useful for the development of optoelectronic and photonic devices (Zhu and Cheng, 2020; Alfurayj et al., 2021). However, the ultrafast carrier dynamics of GaS is rarely addressed.

Herein, we report the nonlinear absorption response and carrier dynamics of a multilayer  $\beta$ -GaS single-crystalline thin film under femtosecond laser excitation. We demonstrate, through femtosecond open-aperture Z-scan measurement, that the nonlinear absorption coefficient of GaS films is  $-1.8 \times 10^{-8}$  m/W and  $4.9 \times 10^{-8}$  m/W under 532 and 650 nm excitation, respectively. And the femtosecond TA data reveal that the carrier relaxation processes in GaS films have two exponential components. The large NLO coefficient and long carrier lifetime of the  $\beta$ -GaS thin films indicate that GaS is a promising candidate for future NLO devices.

## MATERIALS AND METHODS

### Sample

The multilayer  $\beta$ -GaS thin films with a thickness of 800 nm were deposited on a 500  $\mu$ m thick sapphire substrate by atomic layer deposition (ALD) technique (Nanjing MKNANO Technology Co., Ltd). The size of  $\beta$ -GaS film and the sapphire substrate was 5  $\times$  5 and 10  $\times$  10 mm, respectively. The deposited  $\beta$ -GaS films have a hexagonal crystal structure. And the XRD and Raman characterization of  $\beta$ -GaS films can be found elsewhere (Mukenano, 2021).

### DFT Calculation

In our theoretical calculation, we used the experimental hexagonal lattice constant of  $a = 3.626$  Å and  $c = 17.425$  Å. The electronic band structure was based on the DFT with the generalized gradient approximation (GGA) (Perdew et al., 1996). The accurate projector-augmented wave (PAW) method (Blöchl, 1994), as implemented in the Vienna abinitio simulation package (VASP) (Kresse and Furthmüller, 1996), was used. The valence configurations of Ga and S atoms adopted in the present

calculations were  $3d^{10}4s^24p^1$  and  $3s^23p^4$ , respectively. A large plane wave cutoff of 550 eV and the small total energy convergence criterion of  $10^{-5}$  eV were used throughout. Fine Monkhorst-Pack k-meshes of  $24 \times 24 \times 8$  were used for the Brillouin zone integrations.

## Nonlinear Optical Measurements

The ultrafast nonlinear absorption properties of the multilayer  $\beta$ -GaS thin films were measured by open-aperture Z-scan technique. The Z-scan system in this study is similar to the previous report (Shen et al., 2020). In brief, the laser was emitted from an optical parametric amplifier (Light Conversion ORPHEUS) pumped with a Yb:KGW femtosecond fiber laser (Light Conversion PHAROS-SP). The pulse duration and laser repetition rate of the OPA were 190 fs and 20 Hz, respectively. The laser wavelength used in Z-scan measurement were tuned to 532 and 650 nm. The sample placed on the mobile stage was moved along the z-axis with respect to the focal point of a 200 mm focal lens. The laser beams were measured by two energy detectors (Laser probe, Rjp-765) connected to an energy meter (Laser probe, Rj-7620). The Z-scan system was calibrated using a 2 mm thick ZnSe semiconductor.

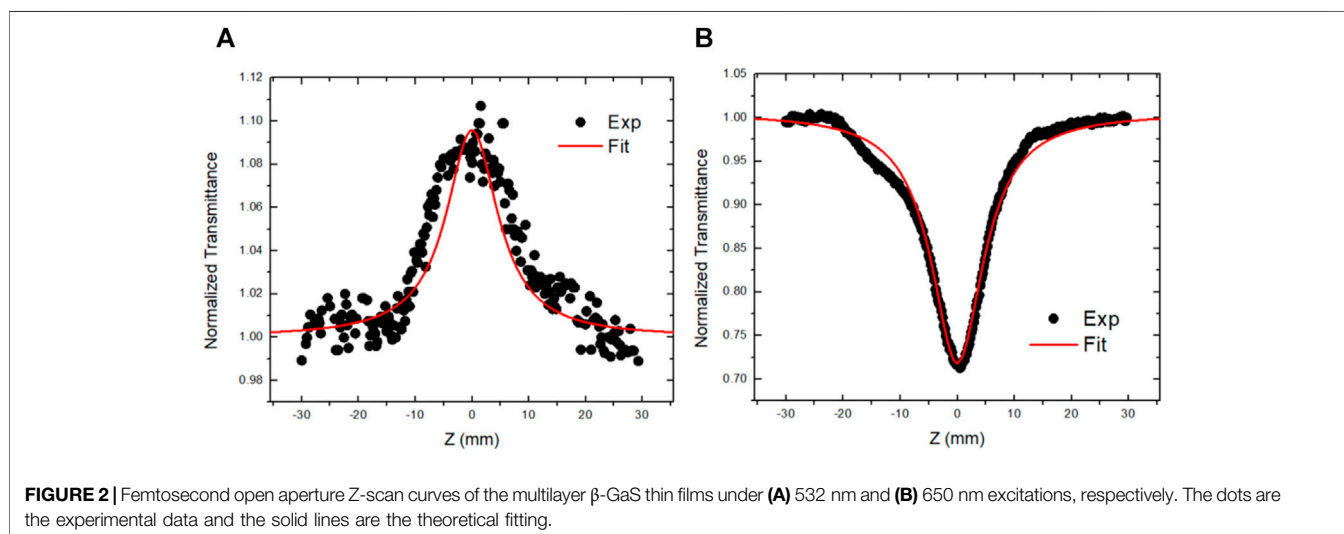
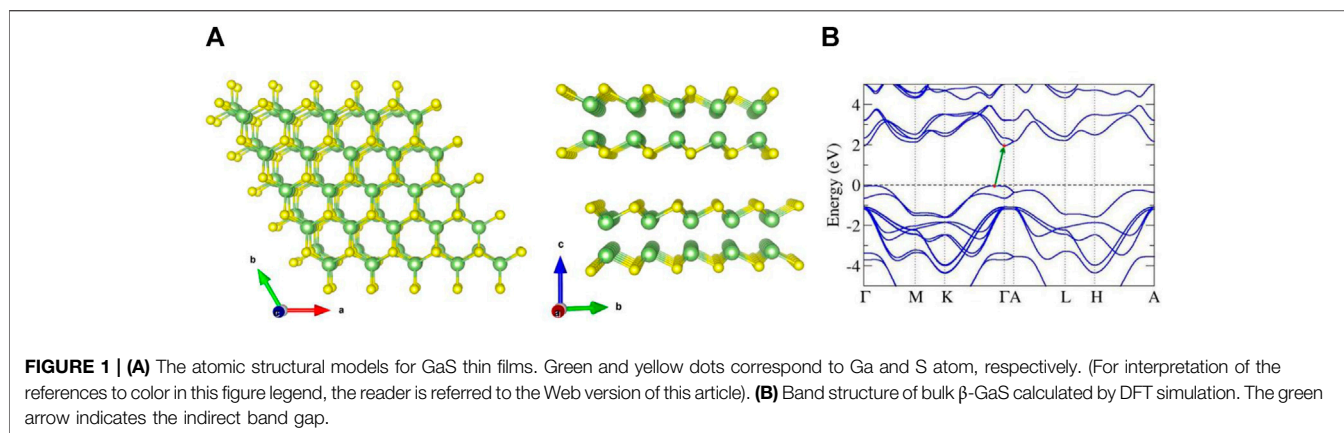
## Femtosecond TA Measurement

The ultrafast carrier dynamics in the multilayer  $\beta$ -GaS thin films were measured by femtosecond transient absorption (TA) spectroscopy. The TA spectroscopy was performed in the two-beam transmission geometry. The laser source was the same in the Z-scan measurements. We used pump wavelengths of 355 nm with photon energy of 3.49 eV, which is larger than the bandgap of  $\beta$ -GaS ( $\sim 2.5$  eV). The pump fluence was kept below 50  $\mu$ J/cm<sup>2</sup> to avoid high-order carrier relaxation processes and thermal damage of the GaS thin films. The probe beam was a white light supercontinuum generated using a sapphire crystal. The pump and probe beam illuminated the films on the front side. The time resolution of the TA measurement system was  $\sim 280$  fs. Details of our TA measurement can be found in the previous report (Li et al., 2021).

## RESULTS AND DISCUSSION

### Atomic Structure

**Figure 1A** shows the atomic structure of bulk  $\beta$ -GaS. It is shown that the  $\beta$ -GaS has a hexagonal lattice, and the stacking type of  $\beta$ -GaS comprises with monolayer consisting of Ga and S in the stacking sequence of S-Ga-Ga-S along the c axis. Therefore, the layered atomic structure of  $\beta$ -GaS is clearly shown. Because of the comparatively large thickness of our  $\beta$ -GaS film ( $\sim 800$  nm), the quantum confinement effect is negligible in the DFT calculation. Therefore, the DFT result of bulk GaS is also applicable to the  $\beta$ -GaS film in this study. The calculated scalar-relativistic band structure of  $\beta$ -GaS is shown in **Figure 1B**. The DFT results demonstrate that the  $\beta$ -GaS is an indirect bandgap semiconductor, which agrees well with previous experimental report (Ho and Lin, 2006).



## Open Aperture Z-Scan

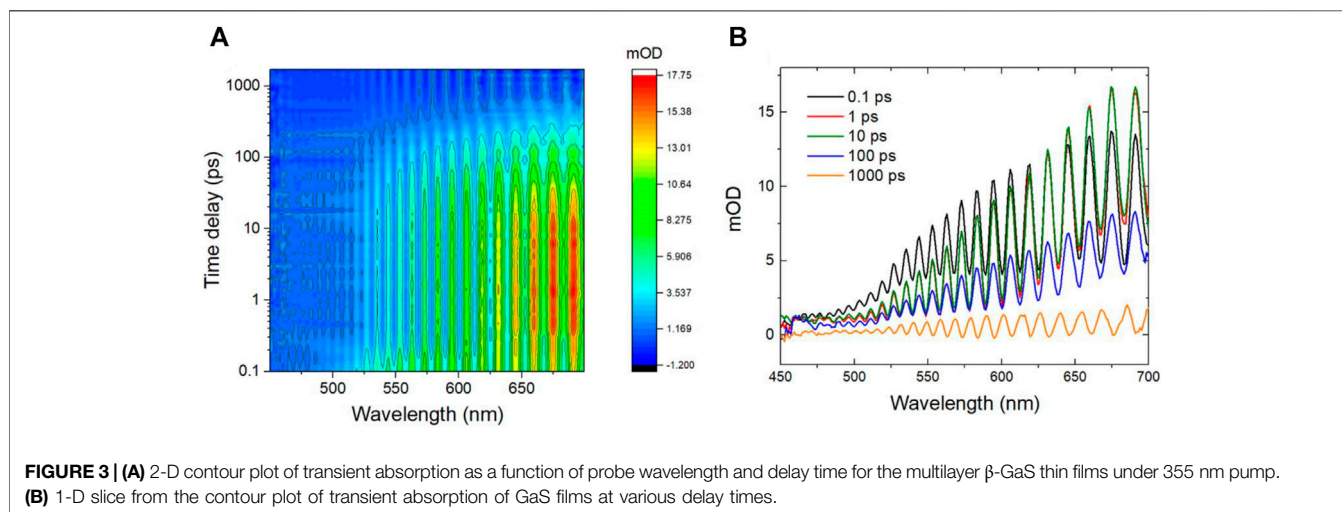
The open aperture Z-scan curves of the multilayer  $\beta$ -GaS thin films measured under 532 and 650 nm excitation were shown in **Figures 2A,B**, respectively. The pulse energy used in Z-scan measurements was 3 and 12 nJ for 532 and 650 nm, and corresponding laser intensity at beam focus was  $1.45 \text{ GW/cm}^2$  and  $3.43 \text{ GW/cm}^2$  for 532 and 650 nm, respectively. The sapphire substrate was also measured under the same experimental condition and found to have negligible nonlinear response. The Z-scan curves in **Figure 2** show that multilayer  $\beta$ -GaS thin films have saturable absorption (SA) behavior at 532 nm, while reverse saturable absorption (RSA) appears under 650 nm excitation. Due to the short pulse duration (190 fs) and low repetition rate of our laser system, the thermal nonlinearity can be negligible in our measurement. The photon energy of light at 532 and 650 nm is 2.33 and 1.91 eV, respectively. Therefore, the  $\beta$ -GaS film ( $E_g \sim 2.5 \text{ eV}$ ) was unable to be excited with one photon with energy of 1.91 eV (650 nm). Hence, the RSA behavior at 650 nm can be attributed to the two-photon absorption mechanism. On the other hand, laser excitation at 532 nm was near-resonant with the bandgap of  $\beta$ -GaS. As a result, the SA behavior at 532 nm could be attributed to the state bleaching of band

edge state or shallow defect state in  $\beta$ -GaS. (Christodoulides et al., 2010). The Z-scan curves were fitted using the standard Z-scan theory (Sheik-Bahae et al., 1990), and the effective nonlinear absorption coefficients were determined to be  $-1.8 \times 10^{-8} \text{ m/W}$  and  $4.9 \times 10^{-8} \text{ m/W}$  for 532 and 650 nm, respectively. Previous results demonstrate that the film thickness has a significant influence on the NLO response of 2D material (Zhang et al., 2018; Verrone et al., 2020). However, the experimental data of  $\beta$ -GaS thin film with different thickness was not available due to the limitation of film deposition system and the low laser damage threshold of few-layer thin film.

The NLO parameters of multilayer  $\beta$ -GaS thin films and various metal monochalcogenide and 2D layered materials reported in recent literatures (Kürüm et al., 2010; Isik et al., 2013; Dong et al., 2016; Ren et al., 2016; Karatay, 2019; Ertap, 2018; Jia et al., 2020) are summarized in **Table 1**. Note that it should be cautious to compare the definite value of NLO coefficients measured at different wavelength and different pulse duration. However, the data in **Table 1** clearly demonstrates that the multilayer  $\beta$ -GaS thin films have excellent nonlinear absorption response. A large  $\beta$  on the order of  $10^{-8} \text{ m/W}$  is observed, which is comparable to the reported values of PdSe<sub>2</sub> and

**TABLE 1** | Summary of the nonlinear absorption coefficients obtained in this study and reported in recent literatures.

Materials	Characterization	Thickness	Bandgap (eV)	Excitation wavelength and pulse duration	$\beta$ (cm/GW)	Ref
GaS	Amorphous film	50 nm	1.41	1,064 nm, 65 ps	662	20
GaS	Bulk crystal	160 $\mu\text{m}$	2.57	1,064 nm, 4 ns	1,520	22
GaSe	Amorphous film	45 nm	0.85	1,064 nm, 65 ps	550	36
GaSe	Bulk crystal	100 $\mu\text{m}$	2.0	1,200 nm, 100 fs	0.182	37
GO	Bulk film	300 nm	0.88	800 nm, 85 fs	7	38
PdSe <sub>2</sub>	polycrystalline	8 nm	0.7	800 nm, 140 fs	3,260	39
WS <sub>2</sub>	Bulk film	58 nm	1.3	1,040 nm, 340 fs	1800	40
$\beta$ -GaS	Single-crystalline film	800 nm	2.5	532 nm, 190 fs	-1800	This work
				650 nm, 190 fs	4,900	



**FIGURE 3** | (A) 2-D contour plot of transient absorption as a function of probe wavelength and delay time for the multilayer  $\beta$ -GaS thin films under 355 nm pump. (B) 1-D slice from the contour plot of transient absorption of GaS films at various delay times.

WS<sub>2</sub> and higher than that of electrochemical graphene oxide (GO) (Dong et al., 2016; Ren et al., 2016; Jia et al., 2020), highlighting the strong NLO effect in the  $\beta$ -GaS film. The large NLO coefficient of  $\beta$ -GaS film could be ascribed to (a) homogeneously deposited film with improved crystalline compared to the amorphous or polycrystalline forms (Kumar et al., 2016), and (b) the ratio of photon energy to bandgap at 650 nm (532 nm) is 0.76 (0.93), which is close to the maximum value of the dispersion curve of  $\beta$  based on two parabolic-band model in semiconductors (Christodoulides et al., 2010). According to the Z-scan data, the imaginary part of the third-order nonlinear susceptibility can be deduced through the equation  $\text{Im}\chi^{(3)} = \frac{n^2 c^2}{240\pi^2 \omega} \beta (m/W)$ . And the figure of merit (FOM) for the third-order optical nonlinearity ( $\text{FOM}_{\text{Im}} = |\text{Im}\chi^{(3)}/\alpha_0|$ ) (Dong et al., 2016) can be determined to be  $-2.7 \times 10^{-13}$  (esu cm) and  $8.9 \times 10^{-13}$  (esu cm) for 532 and 650 nm, respectively. The FOM of  $\beta$ -GaS film is higher than the reported values of WS<sub>2</sub> and Sb<sub>2</sub>Te<sub>3</sub> thin films (Dong et al., 2016; Verrone et al., 2020), indicating the  $\beta$ -GaS is a promising candidate for applications in optical limiting and ultrafast saturable absorber.

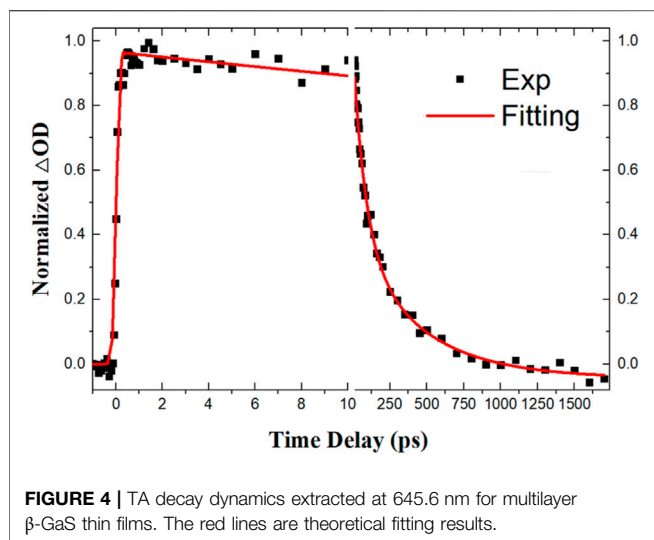
## Femtosecond TA Results

To understand the origin of strong light absorption, ultrafast carrier dynamics in  $\beta$ -GaS thin films were studied with

femtosecond TA spectroscopy. **Figure 3** a and b shows the two-dimensional (2D) contour plot of TA and one-dimensional (1D) slice of TA spectra for the  $\beta$ -GaS thin films under 355 nm excitation, respectively. All TA spectra show periodic interference fringes, which are the characteristics of a highly homogeneous film thickness. Similar results were reported from the measurements of the TA spectra in GaN thin films (Fang et al., 2016). The TA spectra show strong photo-induced absorption (PIA) band around 650 nm, while the amplitude of TA is rather weak below 520. These results agree well with the Z-scan measurements, while could be attributed to the state bleaching around bandgap of  $\beta$ -GaS ( $\sim 2.5$  eV). Moreover, a careful inspection of TA spectra in **Figure 3B** reveals that the TA signals remains almost the same at 1 and 10 ps, then the TA signals decay within hundreds of picoseconds. These results indicate that the  $\beta$ -GaS thin films have long carrier lifetime.

To elucidate the carrier relaxation dynamics in multilayer  $\beta$ -GaS thin films, we have chosen the probe wavelength at 645.6 nm (near the peak of PIA band). The normalized TA decay curve at 645.6 nm of  $\beta$ -GaS thin films under 355 nm excitation is shown in **Figure 4**. It is found that the TA signal rises instantaneously and reaches the maximum at  $\sim 0.3$  ps, which





is limited by our instrument response. The TA signal remains almost constant from 0 to 10 ps, followed by an exponential decay. To analyze the TA results, we used the multi-exponential decay model (Li et al., 2017):

$$\Delta T(t) = \Delta A_0 + \left[ \sum_i A_i \exp\left(-\frac{t}{\tau_i}\right) \right]$$

where  $\tau_i$  and  $A_i$  are the time constants and amplitudes of the decay components, respectively and  $A_0$  is the offset (set as zero in the fitting). The fitting curves are shown as the solid lines in **Figure 4**. The exponential decay analysis indicates that the decay processes in  $\beta$ -GaS thin films consist of two kinetic components with time constants of  $85 \pm 19$  ps and  $450 \pm 50$  ps, respectively. The fast and slow decay components could be attributed to the defect trapping and inter-band carrier recombination in  $\beta$ -GaS thin films, respectively. These results are analogous to that reported for other semiconductor materials (Fang et al., 2016; Li et al., 2017; Kong et al., 2018; Yan et al., 2020; Li et al., 2021). Our TA measurements sheds light on the carrier relaxation mechanism in GaS materials, which could be helpful to develop a clear understanding on the carrier dynamics in Group-III metal monochalcogenide semiconductors.

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## CONCLUSION

In summary, the nonlinear absorption response of multilayer  $\beta$ -GaS thin films prepared *via* ALD was characterized by using open-aperture Z-scan method at femtosecond time regime. The  $\beta$ -GaS thin films show strong saturable absorption and reverse saturable absorption under 532 and 650 nm excitation, which is attributed to the state bleaching and two-photon absorption mechanism. Femtosecond transient absorption spectroscopy reveals that the carrier relaxation dynamics in the  $\beta$ -GaS thin films consist of a fast (tens of picoseconds) and slow (hundreds of picoseconds) processes, which is related to the defect trapping and recombination, respectively. The excellent nonlinear optical coefficient and long carrier lifetime indicate that the metal monochalcogenide GaS is highly promising for applications in optical modulation, optical limiting and solar energy conversion devices.

## DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding authors.

## AUTHOR CONTRIBUTIONS

HL, ZL, and YL contributed conception and design of the study. ZL and YC contributed the testing of samples. HL, KY, and YK performed the DFT simulation. HL wrote the first draft of the manuscript. ZL and YL wrote sections of the manuscript. All authors contributed to manuscript revision, read, and approved the submitted version.

## FUNDING

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (NSFC) (grant no. 62174016) and Suzhou Science and Technology Project (GrantNo.SZS2020313).

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