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Switching from negative to positive nonlinear absorption in *p* type 0.5 at% Sn doped GaSe semiconductor crystal

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ABSTRACT

The nonlinear absorption properties of *p* type 0.5 at% Sn doped GaSe crystal have been studied by using open-aperture Z-scan technique under 1064 nm wavelength and 4 ns or 65 ps pulse duration. A switching from negative nonlinear absorption (saturated absorption) to positive nonlinear absorption (two photon absorption) has been observed as the input laser irradiance increases from 0.049 GW/cm^2 to 0.106 GW/cm^2. The nonlinear absorption coefficient increases monotonically with the increase of pulse duration from 65 ps to 4 ns.

1. Introduction

Layered semiconductors of III–VI groups have been widely studied because of their specific energy bands, interesting crystal structures and highly anisotropic electrical and optical properties [1–4]. GaSe is one of the promising nonlinear crystals for middle-infrared frequency conversion, since GaSe layered crystals have low absorption coefficients in broad optical wavelengths, from near to far-infrared region (0.65–18 μm), and they are transparent through this region [5,6]. The structure of GaSe is characterized by a strong anisotropy in the chemical bonding. Each covalently bonded layer consists of four monoatomic sheets in the order Se–Ga–Ga–Se [1,7]. The single layer is hexagonal and the *c*-axis is perpendicular to the layer plane. The layers are bounded together by weak van der Waals forces. So far, Z-scan experiments of GaSe crystal which have been carried out at 1064 nm wavelength exhibited two photon absorption (TPA). Comprehensive data about TPA coefficients of GaSe are given in the literature [3,8,9]. Existing data on the TPA coefficient of GaSe are not in agreement. Very recently, the TPA coefficient was found to be 1.07×10^{-9} cm/W [8]. Exciton polaritons and biexcitons contribute to the nonlinear optic effects in GaSe crystals [10]. By using Nd:YAG laser with 200 kW/cm^2 power, the biexciton formation was observed as a result of TPA [11,12].

On the other hand, in spite of its many attractive features, GaSe crystal is difficult to be cut and polished along some arbitrarily chosen directions while further improvement in the optical and mechanical properties of GaSe crystal is highly desirable for laser applications. The doping of GaSe crystal seems to be the optimal method to improve its optical and other physical properties. There are markedly many studies carried out to observe the influence of chemical doping in GaSe crystals with different atoms, such as Cl [10], Sn [11,12], Cu [13], Li [14], Zn [15]. An improvement in the optical nonlinearity of GaSe crystal with doping In, Ag or S has been reported [16–18]. GaSe crystals can be both *p* or *n* type semiconductors, depending on growth conditions and dopant atoms. Some physical and optical properties of Sn doped *p* or *n* type GaSe crystals have been reported [11,12,19,20].

In Sn doped GaSe crystals, Ga vacancy and Sn form a donor center with a single electron. These slow recombination centers play important role in photoluminescence and photoconductivity [21,22]. In 0.5 at% Sn doped GaSe crystals, the random distribution of these recombination centers causes oscillation in crystal potential and lead to long time relaxation of photoconductivity [23]. In these Sn doped GaSe crystals the slow recombination centers were found to be in the middle of the band gap (1 eV) while the energy position of the fast recombination centers was found to be $E_v + 0.6$ eV [23]. These crystals can be both *n* type and *p* type depending on the crystal growth regime, dopant atoms and their concentrations. Sn atoms may go into different positions in GaSe lattice and hence crystals can be both *n* type and *p* type [11]. The Sn doped crystals grown in Ref. [12] were *n* type. The donor levels of Sn atoms were found to be 0.52 eV below the conduction band [12]. At low doping concentration Sn behaves as a double acceptor impurity in GaSe with ionization energies of 0.155 eV and 0.31 eV

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[11]. Although some physical and optical properties of Sn doped *p* or *n* type GaSe crystals have been reported [11,12,19,20], the nonlinear optical properties of Sn doped GaSe crystal have not been studied. In this paper, we studied the nonlinear optical absorption of *p* type 0.5 at% Sn doped GaSe crystal using nanosecond and picosecond lasers by the open-aperture Z-scan technique. For the first time, we observed a switching from saturable absorption (SA) to two photon absorption in Sn doped GaSe crystal by increasing input laser irradiances.

2. Experimental

Sn doped GaSe crystals were grown using conventional Bridgman method from a stoichiometric mixture of high purity Ga (99.9999%) and Se (99.999%) in evacuated quartz ampoules (10^{-4} Torr) whose inner walls were coated with graphite [24]. Sn doping was done by adding the 0.5 at% Sn to initial batch composition. Ingots were cleaved perpendicular to *c*-axis using a razor blade. The thickness of Sn doped GaSe crystal used for Z-scan measurements was measured to be 93.2 μm with a camera connected optic microscope (Nikon-OPTIPHOT-100).

The UV–Vis absorption spectrum of the Sn doped GaSe crystal was recorded using a scanning spectrophotometer (Shimadzu UV-1800) at room temperature (300 K).

The nonlinear absorption of 0.5 at% Sn doped GaSe crystal was examined by open-aperture Z-scan method. This technique is a simple and sensitive experimental technique for the study of nonlinear optical properties and allows determining the sign of the nonlinear refractive and absorption indices. In this study, the open-aperture Z-scan experiments were carried out with nano- and picosecond laser sources. For the nanosecond (ns) and picosecond (ps) open-aperture Z-scan experiments, the light sources were Q-switched Nd:YAG laser with pulse duration of 4 ns (Quantel Brillant) and pulse duration of 65 ps (Continuum Leopard SV). The lasers were operated at a wavelength of 1064 nm and a repetition rate of 10 Hz. All Z-scan measurements reported here were carried out at room temperature. The radiation for both nanosecond and picosecond Z-Scan experiments was focused by a 200 mm focal length lens.

3. Results and discussions

The room temperature linear absorption spectrum of the 0.5 at% Sn doped GaSe crystal whose nonlinear optic properties are being investigated is given in Fig. 1. The sharply increasing of absorption edge shows that this crystal does not contain any impurity. As seen, the linear absorption spectrum starts with the $n = 1$ direct exciton absorption even at room temperature. Several investigations showed that the long wavelength tail of the exciton absorption has an exponential dependence to photon energy according to Urbach–Martienssen rule [24,25]. The long wavelength tail of the absorption spectra in Fig. 1 has been studied using this theory and the theoretical fit is given as a solid line in the inset of Fig. 1. As a result of exciton–phonon, exciton–dopant atoms the Urbach energy is calculated to be 0.013 eV while the FWHM of the exciton peak is calculated to be 0.021 eV.

Nonlinear absorption can be classified into two types: first, transmittance increases with increasing optical intensity; this nonlinear absorption corresponds to SA. Second, transmittance reduces with increasing optical intensity; this nonlinear absorption includes TPA, multiphoton absorption, and reverse saturable absorption (RSA). Typical results of the open-aperture Z-scan measurements for an irradiation wavelength of 1064 nm with 4 ns or 65 ps pulse duration are shown in Figs. 2 and 3, respectively. Nanosecond and picosecond open-aperture Z-scan

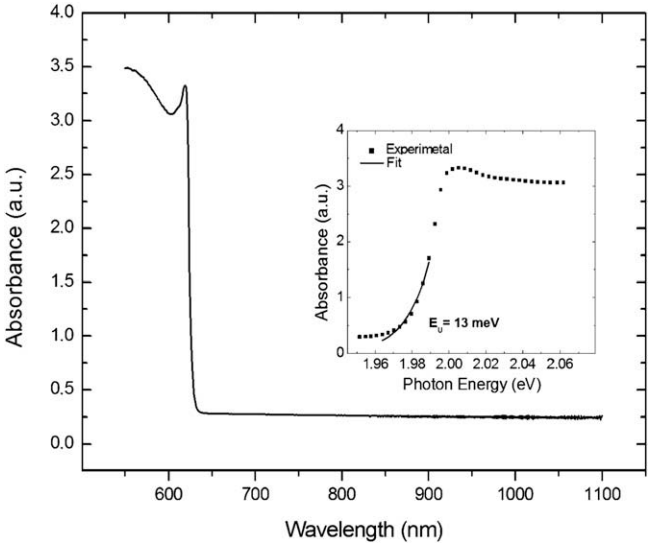

Fig. 1. Linear absorption spectrum of the 0.5 at% Sn doped GaSe crystal. The inset shows the Urbach fit (given as solid line) of the long wavelength tail of the absorption.

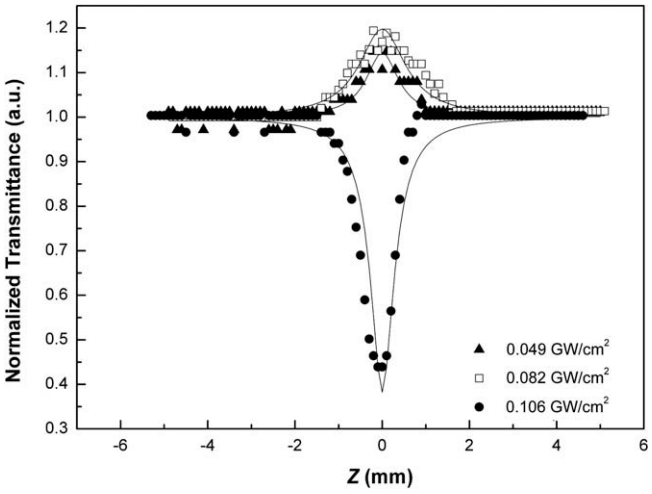

Fig. 2. Relative transmission at 1064 nm and 4 ns pulse duration of the 0.5 at% Sn doped GaSe crystal.

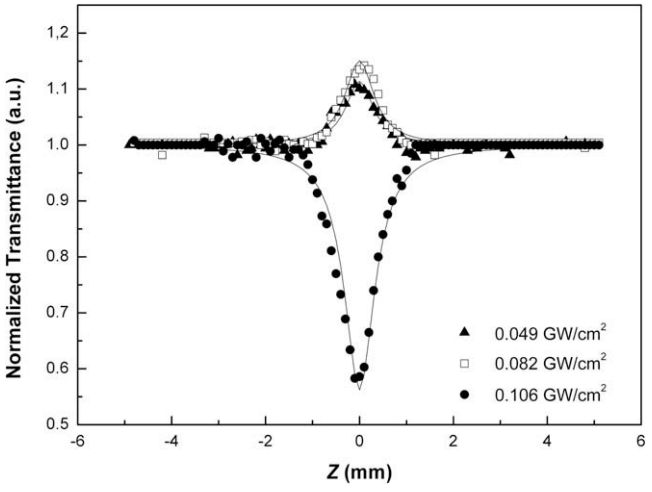

Fig. 3. Relative transmission at 1064 nm and 65 ps pulse duration of the 0.5 at% Sn doped GaSe crystal.