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The effect of Se/Te ratio on transient absorption behavior and nonlinear absorption properties of $CuIn_{0.7}Ga_{0.3}(Se_{1-x}Te_x)_2$ $(0 \le x \le 1)$ amorphous semiconductor thin films

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ABSTRACT

The characterization of the $CuInSe_2$ (CIS), CuInGaSe (CIGS) and $CuGaSe_2$ (CGS) based semiconductor thin films are very important role for solar cell and various nonlinear optical applications. In this paper, the amorphous $CuIn_{0.7}Ga_{0.3}(Se_{1-x}Te_x)_2$ semiconductor thin films $(0 \le x \le 1)$ were prepared with 60 nm thicknesses by using vacuum evaporation technique. The nonlinear absorption properties and ultrafast transient characteristics were investigated by using open aperture Z-scan and ultrafast pump-probe techniques. The energy bandgap values were calculated by using linear absorption spectra. The bandgap values are found to be varying from 0.67 eV to 1.25 eV for $CuIn_{0.7}Ga_{0.3}Te_2$, $CuIn_{0.7}Ga_{0.3}Se_{1.6}Te_{0.4}$, $CuIn_{0.7}Ga_{0.3}Se_{0.4}Te_{1.6}$ and $CuIn_{0.7}Ga_{0.3}Se_2$ thin films. The energy bandgap values decrease with increasing telluride (Te) doping ratio in mixed $CuIn_{0.7}Ga_{0.3}(Se_{1-x}Te_x)_2$ films. This affects nonlinear characteristics and ultrafast dynamics of amorphous thin films. Ultrafast pump-probe experiments indicated that decreasing of bandgap values with increasing the Te amount switches from the excited state absorption signals to ultrafast bleaching signals. Open aperture Z-scan experiments show that nonlinear absorption properties enhance with decreasing bandgaps values for 65 ps pulse duration at 1064 nm. Highest nonlinear absorption coefficient was found for $CuIn_{0.7}Ga_{0.3}Te_2$ thin film due to having the smallest energy bandgap.

1. Introduction

Optoelectronic properties of semiconductors have generated a lot of research and technological interest because of their novel applications in different devices such as solar cells, light emitting diodes (LED), laser diodes (LD), integrated circuits (IC), photo detectors (PD), nanotechnology, heterostructure lasers and optical modulators. An increased knowledge of semiconductor materials and fabrication processes has made possible continuing increases in the wide range applications. One of the important interest is the ability to improve efficiency of solar cells for the production of the commercially suitable modules. Many studies reported that I-III-V2 based semiconductors such as $CuInSe_2$ (CIS), CuInGaSe (CIGS) and $CuGaSe_2$ (CGS) thin films are preferred for solar cell applications due to the their high efficiencies [1–7]. CIGS based materials prevent waste of raw materials thanks to having strong photo absorption properties in very thin layer (~1–2 μm) with respect to crystal forms [8–10]. Very recently the electrical properties of these materials have been characterized [11,12]. On the other hand, nonlinear optical properties of semiconductor thin films have been extensively studied due to their wide applications such as Q-switching, mode-locking [13,14], optical limiting [15] and upconversion lasing [16].

Recently, we studied structural, electrical (diode properties) [11,12] and optical properties of CuIn, CuGa and Ga/(In + Ga) based materials [9]. According to our results, we have found that when we change the Se/Te ratio, the bandgap changes from 1 to 1.5 eV in CuIn samples. On the other hand, when we change the Se/Te ratio, the bandgap changes from 1.23 to 1.70 eV in CuGa samples. Theoretically, the bandgap value changes from 1.02 to 1.72 eV in Ga/(In + Ga) structure [9]. Our motivation is that making a four joined

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structure using a single type material. On the other hand, we investigated the structural and diode characteristics of these materials. We determined the optimal composition according to electrical characteristics. Our aim is to study nonlinear optical properties of this composition $CuIn_{0.7}Ga_{0.3}(Se_{1-x}Te_x)_2$ with the effect of doping ratio of Se/Te.

Preparation of the CIGS films with the predetermined composition requires a good control over the deposition process such as co-evaporation [17], sputtering [18,19], molecular beam epitaxy [20], metal organic chemical vapor deposition [21], spray pyrolysis [22], electrodeposition [23], pulsed laser deposition [24] and so on. The studied CIGS films in literature are polycrystalline with defects at grain boundaries [25]. Here we embark upon research into the linear and NLO properties of $CuIn_{0.7}Ga_{0.3}(Se_{1-x}Te_x)_2$ amorphous thin films ($0 \le x \le 1$) with 60 nm thicknesses. The investigated amorphous thin films were directly prepared from mixed semiconductor crystals by using vacuum evaporation. The nonlinear optical characteristics of amorphous CIGS films are expected to depend critically on composition and deposition process. In general, nonlinear absorption (NA) and saturable absorption (SA) characteristics of amorphous very thin films depend on the inherent properties of a material and the parameters such as the life time of the localized defect states, saturation intensity threshold, and pulse duration of the laser used. Our previous studies showed that the saturation threshold can be changed by altering the film thickness and/or doping. In an attempt to find the effect of composition on the saturation threshold, we studied the SA properties of very thin single layer of $CuIn_{0.7}Ga_{0.3}(Se_{1-x}Te_x)_2$ amorphous thin films ($0 \le x \le 1$) with 60 nm thicknesses amorphous semiconductors with OA Z-scan and pump–probe techniques.

NA and SA are defined as a increase or reduction of the absorption coefficient with increasing optical intensity respectively. SA materials have been used extensively in short-pulsed laser generations [26] as crucial passive mode-locking or Q-switching elements. There is a significant demand for thin film nonlinear optical materials showing SA behavior with controllable saturation intensity threshold and response time. It is well known that the line and planar defects in the polycrystalline thin films and the crystalline size effect can lead to change energy band gap [27]. On the other hand, in amorphous semiconductor thin films, one photon absorption (OPA), two photon absorption (TPA) and free carrier absorption (FCA) can contribute nonlinear absorption behavior. Previously, we investigated the effect of thickness dependence on the nonlinear absorption properties of amorphous InSe and GaSe thin films [28,29]. Our previous results indicated that the nonlinear absorption properties are very sensitive to the film thickness. The aim of this study is to investigate the effect of doping ratio of Se/Te on energy bandgap and nonlinear absorption properties amorphous thin films with 60 nm thicknesses.

2. Experimental

In fabrication process, $CuIn_{0.7}Ga_{0.3}(Se_{1-x}Te_x)_2$ (x = 0, 0.2, 0.8 and 1) compound ingots were prepared from a stoichiometric mixture of pure elements. Stoichiometric amounts of the individual elements, copper, indium, gallium, selenium and tellurium are sealed in a coated carbon quartz ampoule at 1×10^{-6} Torr. The quartz ampoule with the mixture of elements is placed in a furnace, which is heated at a rate of 100 °C per hour up to 1100 °C and kept at this temperature for 24 h in order to homogenize the molten mixture, during the process of heating, the ampoule is continuously rotated. The quartz ampoule is then allowed to cool slowly at rate of 100 °C/h to room temperature.

Amorphous thin films of $CuIn_{0.7}Ga_{0.3}Se_2$, $CuIn_{0.7}Ga_{0.3}Se_{1.6}Te_{0.4}$, $CuIn_{0.7}Ga_{0.3}Se_{0.4}Te_{1.6}$ and $CuIn_{0.7}Ga_{0.3}Te_2$ from mixed semiconductor crystals were prepared by vacuum evaporation technique at 1×10^{-6} Torr [28,29]. The film thicknesses were determined to be 60 nm by using spectroscopic ellipsometer (Woollam, -M2000V) with the same procedure described before [30]. The absorption spectra of the investigated amorphous films were recorded by using a UV–Vis absorption spectrophotometer (Shimadzu UV-1800). An uncoated fused silica substrate was used as a reference. In order to investigate the nonlinear absorption mechanism and ultrafast dynamics of the studied films transmission pump-probe spectroscopy technique was used with the help of Ti:sapphire laser amplifier optical parametric amplifier system (Spectra Physics, Spitfire Pro XP, TOPAS) with 100 fs pulse duration. The excitation (pump beam) wavelength was chosen as 800 nm for the pump-probe experiments with white light continuum as a probe beam (Spectra Physics, Helios).

The nonlinear optical absorptions properties of investigated amorphous films were determined by open aperture (OA) Z-scan technique [31] using picosecond laser with 1064 nm wavelength, 65 ps pulse duration and 10 Hz frequency. The laser beam was focused on the films with a focal length of 20 cm.

3. Result and discussion

3.1. Linear optical properties

Linear absorption spectra of $CuIn_{0.7}Ga_{0.3}Se_2$, $CuIn_{0.7}Ga_{0.3}Se_{1.6}Te_{0.4}$, $CuIn_{0.7}Ga_{0.3}Se_{0.4}Te_{1.6}$ and $CuIn_{0.7}Ga_{0.3}Te_2$ thin films with 60 nm thicknesses are given in Fig. 1a. The energy bandgap values were calculated from the linear absorption spectra. The $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ plots where α is the absorption coefficient and $h\nu$ is the photon energy was used to determine energy bandgap of the films as seen in Fig. 1b.

The theory of interband absorption shows that the absorption coefficient α has the following dependence on the incident photon energy $h\nu$ at the absorption edge [32].

$$\alpha = \frac{A}{h\nu}(h\nu - E_g)^n \tag{1}$$

where A is a constant, E_g is the optical bandgap and n assumes values of 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. In Fig. 1b indicates that extrapolation of the linear regions on the energy axis was used to determine energy bandgap of studied films which were found as 1.25 eV, 1.07 eV, 0.83 eV and 0.67 eV for $CuIn_{0.7}Ga_{0.3}Se_2$, $CuIn_{0.7}Ga_{0.3}Se_{1.6}Te_{0.4}$, $CuIn_{0.7}Ga_{0.3}Se_{0.4}Te_{1.6}$ and $CuIn_{0.7}Ga_{0.3}Te_2$ thin films, respectively. There is significant energy difference among the films and it depends on the Se/Te doping ratio. Increasing of the Te amount causes a decrease of the energy band gap of the films. These results indicate that energy bandgap can be controlled by changing Se/Te ratio in $CuIn_{0.7}Ga_{0.3}(Se_{1-x}Te_x)_2$ mixed semiconductors [8–10].

3.2. Ultrafast transmission pump-probe experiments

Investigation of carrier dynamics of semiconductors are very important for electronic and optoelectronic applications. In order to identify the effect of Se/Te doping ratio on nonlinear absorption mechanisms for $CuIn_{0.7}Ga_{0.3}(Se_{1-x}Te_x)_2$ thin films. Ultrafast pump-probe experiments were performed at 800 nm pump wavelength to investigate effect of Se/Te doping ratio on the nonlinear absorption mechanism. Transient absorption spectra of investigated films are given in Fig. 2.

Interestingly, transient absorption characteristics of thin films are very different from each other. Continuous excited state