

## TRANSIENT ABSORPTION OF COPPER SELENIDE NANOWIRES OF DIFFERENT STOICHIOMETRY

G. Juška<sup>a</sup>, V. Gulbinas<sup>a</sup>, and A. Jagminas<sup>b</sup>

<sup>a</sup> *Institute of Physics, Center for Physical Sciences and Technology, Savanorių 231, LT-02300 Vilnius, Lithuania*  
E-mail: ged.juska@gmail.com

<sup>b</sup> *Institute of Chemistry, Center for Physical Sciences and Technology, A. Goštauto 9, LT-01108 Vilnius, Lithuania*

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Copper selenide nanowires of different stoichiometric compositions and having different density of defects that form intraband states embedded in a porous alumina layer have been investigated by means of a femtosecond absorption pump-probe technique. Depending on the formation conditions, different samples have different absorption spectra in the near-infrared spectral range, but all of them show bleaching of the most intense absorption bands, which competes with the induced absorption of free charge carriers. A transient absorption relaxation takes place in two steps, with time constants of about 1 ps and several tens of ps. Relative contribution of the fast relaxation component increases in samples with the higher density of defect states forming the recombination centres.

**Keywords:** copper selenide nanowires, transient absorption

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### 1. Introduction

Nonstoichiometric copper selenide  $\text{Cu}_{2-x}\text{Se}$  ( $x = 0-0.25$ ) is a self-doping superionic  $p$ -type semiconductor with a density of free holes normally exceeding  $10^{22} \text{ cm}^{-3}$  [1–3]. A wide range of copper selenide stoichiometric ( $\text{Cu}_2\text{Se}$ ,  $\text{Cu}_3\text{Se}_2$ ,  $\text{CuSe}_2$ ,  $\text{CuSe}$ ) and nonstoichiometric ( $\text{Cu}_{2-x}\text{Se}$ ) compositions and their crystallographic forms have been synthesized and characterized during several decades [4, 5]. The band gap of copper selenide is not well defined because of the wide variety of stoichiometric forms, presence of high density of dislocations and defects, energy barrier height variations in grains of polycrystalline films, and quantum confinement effects [6].  $\text{Cu}_{2-x}\text{Se}$  is usually reported to possess a direct band gap of 2.21–2.39 eV and an indirect band gap of 1.2–1.7 eV [7–9]. Thin films of copper selenide are of particular interest for formation of heterojunction solar cells where they are used as absorbing [10] or window [11] layers. Copper selenide is a precursor material of  $\text{CuInSe}_2$ , used for highly efficient photovoltaic elements [5, 12]. Attempts of application of copper selenide for optical filters [13], saturable absorbers for a passive mode locking of near-IR solid-state lasers [14], humidity sensors [15], highly effective hole injection layers for use with  $p$ -type organic semiconductors [3], novel nanotubes [16] have also been recently reported.

Application of copper selenide for more sophisticated devices requires full-scale characterization of the material. Ultrafast relaxational processes that are essential for nonlinear optical elements and novel electronic nanodevices are barely investigated in copper selenide. Our investigations presented in this paper were stimulated by a very wide dispersion of steady-state optical parameters of copper selenide that indicate presumably different energetic structures and relaxation mechanisms of nonequilibrium photogenerated carriers. Our previous study of nonstoichiometric  $\text{Cu}_{2-x}\text{Se}$  nanowires [17] revealed bleaching of the near-infrared (IR) absorption band and ultrafast transient absorption dynamics. Here we present transient absorption investigations of copper selenide nanowires with different stoichiometric compositions and different defect densities obtained by varying the material synthesis and post-formation treatment. We demonstrate that linear and nonlinear optical properties of copper selenide nanowire arrays loaded inside alumina template pores by electrodeposition crucially depend on the nanowire composition.

## 2. Experiment

The samples under investigation were densely packaged nanowire arrays of a dominant nonstoichiometric  $\text{Cu}_{2-x}\text{Se}$  ( $x \sim 0.25$ ) or stoichiometric  $\text{Cu}_3\text{Se}_2$  fabricated inside alumina pores by an alternating current electrodeposition. In preparation of alumina templates, Al foil (99.99% purity, 100  $\mu\text{m}$  thickness) specimens were annealed at 500 °C for 3 hours, etched in 1.5 M NaOH at 60 °C for 30 s, electropolished in an ethanol (EtOH) solution of perchloric acid and glycerol at 17 V dc for 3 min, and thoroughly rinsed in an EtOH and distilled water. The oxide film formed during electropolishing was removed from the substrate by etching in a 0.24 M  $\text{Na}_2\text{CO}_3$  solution at 80 °C for 60 s. Anodization was performed in thermostated and vigorously stirred electrolytes either of 1.2 M  $\text{H}_2\text{SO}_4$  (10 °C, 15 V) or 0.3 M  $\text{H}_2\text{C}_2\text{O}_4$  (17 °C, 40 V) until the alumina matrix of about 10  $\mu\text{m}$  thickness was grown. The specimens were sonicated in 0.5 M  $\text{H}_3\text{PO}_4$  at 30 °C for 25 min to widen the pores. The as-anodized samples were washed with DI water and incubated in a bath for an electrochemical deposition of copper selenide nanowire arrays. A custom-made supply of an alternating current (ac, 50 Hz) allowing us a simple control of the average current strength was used in the deposition set-up. Nonstoichiometric copper selenide  $\text{Cu}_{2-x}\text{Se}$  nanowires were grown using sulfuric acid alumina matrices (average  $\phi_{\text{pore}}$  15 nm) in 0.03  $\text{CuSO}_4$ , 0.015  $\text{H}_2\text{SeO}_3$ , 0.05  $\text{MgSO}_4$  (in M), and  $\text{H}_2\text{SO}_4$  solution under 0.6 and 0.4  $\text{A dm}^{-2}$  (pH 1.9) and 0.2  $\text{A dm}^{-2}$  (pH 1.4) conditions. These specimens are referred to in this paper as Samples 1, 2, and 3, respectively. For a deposition of quite pure  $\text{Cu}_3\text{Se}_2$  phase nanowires in the oxalic acid alumina template pores ( $\phi_{\text{pore}}$  48 nm) an aqueous solution composed of 0.033  $\text{CuSO}_4$ , 0.015  $\text{H}_2\text{SeO}_3$ , 0.03  $\text{Al}_2(\text{SO}_4)_3$  (in M), and  $\text{H}_2\text{SO}_4$  (to adjust the pH to 1.15), pre-electrolyzed by the alternating current, was used. This sample is referred to as Sample 4. Thermal treatment of the samples was conducted in an open programmable oven (*Zhermack*) within 150 to  $350 \pm 2$  °C temperature range for 60 min.

X-ray diffraction (XRD) and optical investigations were carried out after detaching alumina templates encased with copper selenide nanowires from the substrate by till-side etching of aluminum in an acidic 0.1 M  $\text{CuCl}_2$  solution. X-ray diffraction studies were performed with the diffractometer D8 (Bruker AXS, Germany) equipped with a Göbel mirror for Cu  $\text{K}_\alpha$  radiation. A step-scan mode was used in a  $2\theta$  range from 18 to 55° with a step of 0.04° and a counting time of 15 s per step.

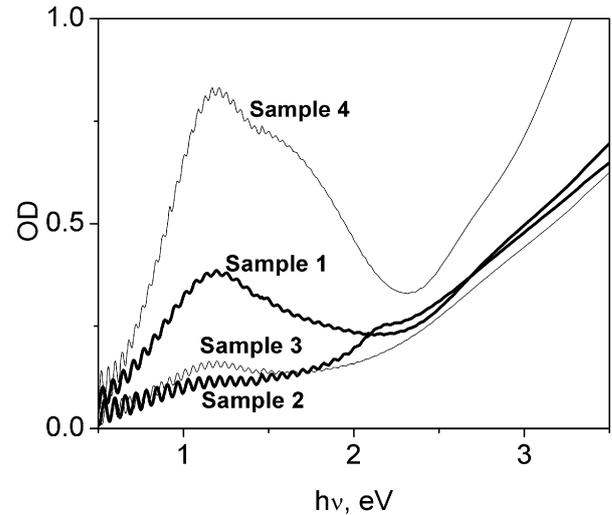


Fig. 1. Steady-state absorption spectra of 48 nm  $\text{Cu}_3\text{Se}_2$  (Sample 4) and 15 nm diameter  $\text{Cu}_{2-x}\text{Se}$  (Samples 1, 2, and 3) nanowires.

Copper selenide nanowires embedded in a porous alumina layer were investigated by means of ultrafast transient absorption technique. A conventional femtosecond two-beam pump-probe spectrometer based on a passively-mode locked amplified Ti:sapphire laser with the pulse duration of 120 fs (FWHM) and the repetition rate of 1 kHz was used. A fundamental laser radiation was used to pump the *Light Conversion* parametric amplifier TOPAS. The samples were excited with 1.65 or 2.88 eV photon energy pulses and induced optical nonlinearities were probed with a white-light continuum generated in a sapphire crystal.

## 3. Results and discussion

Steady-state absorption spectra of the investigated nanowires are presented in Fig. 1. A broad absorption band present in the near-infrared spectral region right below the edge of the fundamental absorption band is a common feature of nanostructures containing double valence copper (e. g.  $\text{CuSe}$ ,  $\text{CuFeS}_2$ ) [13, 18, 19]. Middle-gap states are formed in these compositions and thus the additional low energy absorption band shall be attributed to electron transitions from these states to the conduction band. It is obvious from the steady-state absorption spectra that variations of the electrodeposition parameters and post-deposition treatment result in distinct optical properties of each sample. It was demonstrated that the peak intensity of the absorption band related to the middle-gap states depends on the degree of the sample oxidation [20] and its energetic position can be tuned within the spectral range of 0.8–1.25 eV [14, 21]. The sample annealing causes the most no-

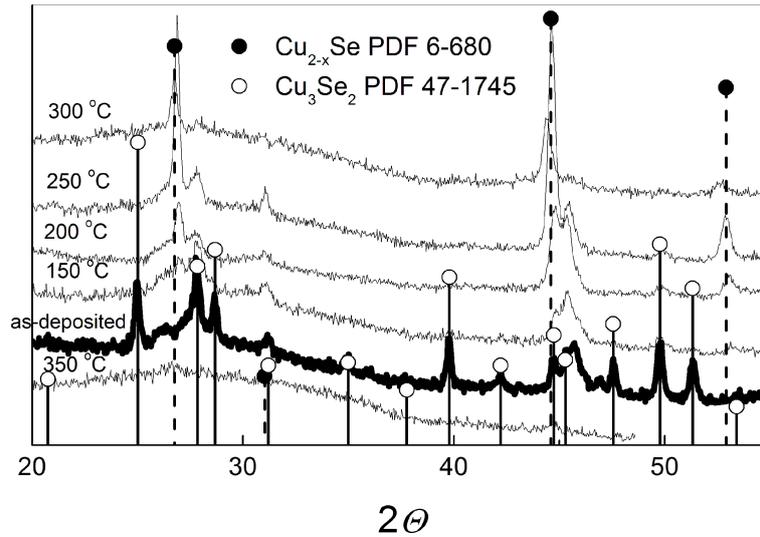


Fig. 2. XRD patterns of oxalic acid alumina template encased with copper selenide nanowires ( $\varnothing_{\text{pore}}$  48 nm) by ac deposition in the solution (M): 0.033  $\text{CuSO}_4$ , 0.015  $\text{H}_2\text{SeO}_3$ , 0.03  $\text{Al}_2(\text{SO}_4)_3$ , and  $\text{H}_2\text{SO}_4$  (down to pH 1.15) at  $0.5 \text{ A dm}^{-2}$  for 45 min before and after annealing in air at indicated temperatures for one hour.

table post-formation treatment effects. The XRD profiles presented in Fig. 2 demonstrate the transformation of the copper selenide stoichiometry induced by the sample annealing. A crystalline tetragonal  $\text{Cu}_3\text{Se}_2$  phase identified by 12 well-defined peaks dominates right after the deposition. Annealing of the nanostructures causes transformation of the  $\text{Cu}_3\text{Se}_2$  phase into the  $\text{Cu}_{2-x}\text{Se}$  phase. The  $\text{Cu}_{2-x}\text{Se}$  phase dominates in samples annealed for 3 hours at 300 °C. A part of the absorption spectrum below the absorption edge of as-deposited 48 nm diameter nanowires (Sample 4) may be well approximated by the superposition of two Lorentzian shape bands with the peak maxima at 1.12 and 1.67 eV and FWHM of 0.61 and 1.48 eV, respectively. As demonstrated in [22], the near-infrared absorption band with the maximum at  $\sim 1.12$  eV belongs to the nonstoichiometric  $\text{Cu}_{2-x}\text{Se}$  phase. Even a small fraction of this phase undetectable by XRD is sufficient to form the absorption band (Fig. 1). Several investigated samples (1, 2, and 3) filled with  $\text{Cu}_{2-x}\text{Se}$  possess slightly different steady-state optical features due to the alternation of their synthesis procedures. The second band at 1.67 eV shall be attributed to the  $\text{Cu}_3\text{Se}_2$  phase. It appears that a lower current density used during the electrochemical deposition of the material leads to the formation of smaller density of the middle-gap states that are responsible for the low energy absorption band, though the intrinsic absorption remains unaffected. Sinusoidal absorption modulations prominent in the infrared region are obviously due to the optical interference effects in a thin alumina layer.

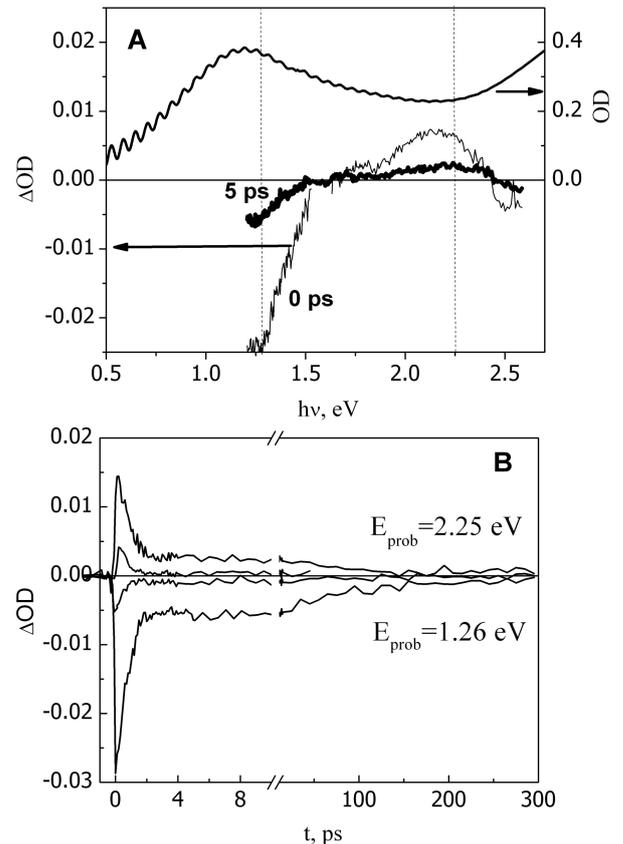


Fig. 3. (a) Transient absorption spectra and (b) kinetics of the Sample 1. Dashed lines in (a) indicate the spectral position of probed kinetics. Optical changes in the sample were induced by 2.26 eV photon energy and  $0.3 \text{ mJ/cm}^2$  (higher intensity curves) or  $0.063 \text{ mJ/cm}^2$  energy density pulses.

Transient absorption spectra and kinetics of a copper selenide obtained in different samples under 2.88 eV

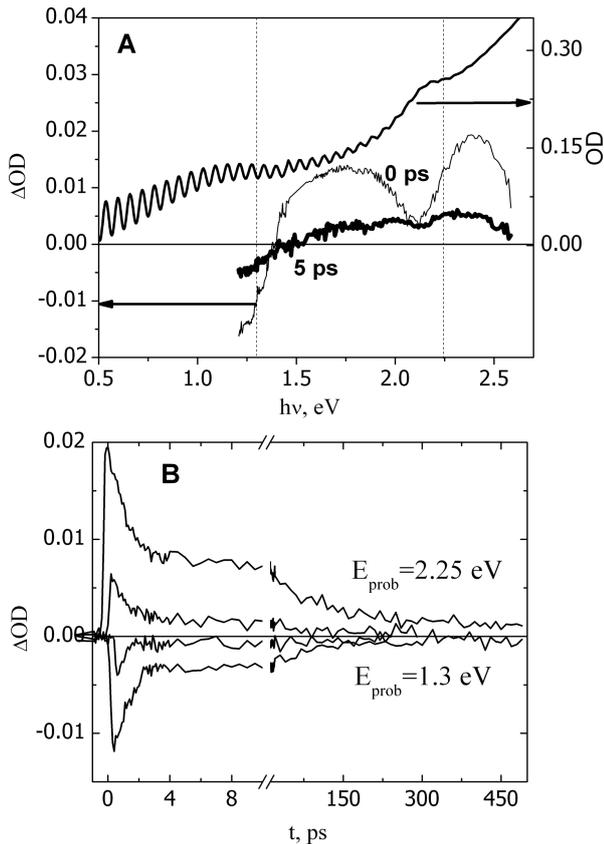


Fig. 4. (a) Transient absorption spectra and (b) kinetics of the Sample 2. Dashed lines in (a) indicate the spectral position of probed kinetics. Optical changes in the sample were induced by 2.26 eV photon energy and 0.3 mJ/cm<sup>2</sup> (higher intensity curves) or 0.063 mJ/cm<sup>2</sup> energy density pulses.

excitation photon energy are presented in Figs. 3–5. Transient absorption spectra and kinetics in nanowires excited with lower energy photons (1.65 eV) were very similar, therefore not presented. A similar weak dependence on the excitation photon energy of the transient absorption properties of a copper selenide was also reported in [17]. We have suggested that during the first 100 fs the nonequilibrium carriers thermalize and relax through the high density manifold of local states to the same energy distribution independently of the initially created state.

Transient absorption spectra of Sample 1 with 15 nm diameter nanowires are presented in Fig. 3(a). This sample has a clearly expressed steady state absorption band in the near-infrared region. The transient absorption spectra indicate that at least two main concurrent nonlinear optical effects of a similar importance, namely absorption bleaching and excited state absorption, compete and cause negative or positive absorbance changes in different spectral regions. Bleaching of the additional absorption band at 1.2 eV dominates in

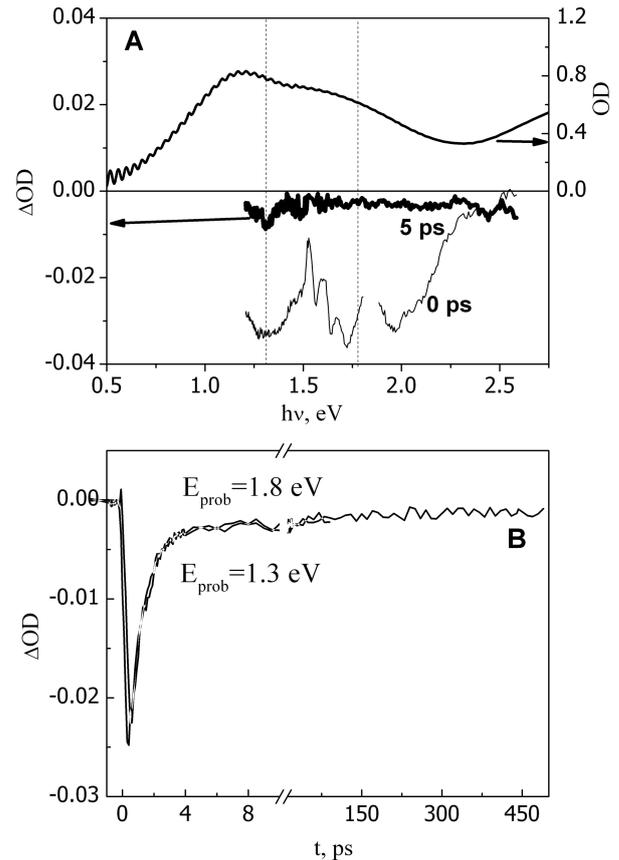


Fig. 5. (a) Transient absorption spectra and (b) kinetics of the Sample 4. Dashed lines in (a) indicate the spectral position of probed kinetics. Optical changes in the sample were induced by 2.26 eV photon energy and 0.3 mJ/cm<sup>2</sup> energy density pulses.

the IR region. The bleaching is clearly caused by the conduction band state filling as presumable transitions from the middle-gap states to the conduction band are blocked. An induced absorption dominates in the visible spectral range. We assume that the absorption by free carriers gives rise to the induced absorption. The differential absorption spectrum measured at 5 ps delay time has basically the same shape. This indicates that either only two transient species are involved in the relaxation process or that material absorbance in some intermediate state is very similar to that in the initially excited state.

Figure 3(b) shows the transient absorption kinetics probed at 1.25 and 2.26 eV in Sample 1 at two different excitation intensities. Transient absorption kinetics indicate complex relaxation process. The rise of the transient absorption changes is very fast, limited by the time resolution of the experimental set-up. The fast initial decay followed by the slower one indicates at least two relaxation mechanisms. Characteristic relaxation time constants were obtained by fitting kinetics with a biexponential decay function. Comparison of the decay pa-

rameters confirms visual similarity of the decay kinetics probed at 2.25 and 1.26 eV. Similar shapes of the transient absorption spectrum at different delay times and similar kinetics in different spectral regions confirm that relaxation of the induced optical changes is mainly mediated by a nonequilibrium carrier recombination. In the case of the maximal excitation intensity, the initial and slower relaxation components are characterized by 0.71 and 120 ps time constants respectively. The induced optical changes relax to about 1/5 of the initial value during the fast relaxation. At lower excitation intensity the initial relaxation is slightly faster, of about 0.55 ps, and the slow component is very weak or barely exists.

The transient absorption spectra and kinetics are in agreement with the energy scheme of copper selenide nanoparticles containing double valence copper as suggested in [17, 20, 23, 24]. This scheme suggests the presence of two intermediate energy levels of different types: deep recombination levels and shallow trapping levels. The scheme reasonably explains the nature of the fast and slow relaxation components. The initial fast relaxation rate and its relative amplitude are mediated by the concentration of deep recombination centres. Saturation of this recombination channel at high excitation intensity leads to population of the long-lived trapping states, and the slow relaxation component appears.

Transient absorption data of Sample 2 with a weakly expressed IR absorption band are presented in Fig. 4. Despite obvious differences of the steady-state absorption spectra between Samples 1 and 2, transient absorption properties are quite similar. An induced absorption dominates in the visible spectral region and an absorption bleaching band appears in the near-infrared region. It indicates that a notably lower concentration of the middle-gap states is still sufficient to yield a strong bleaching effect. The isosbestic point is red shifted to 1.4 eV. The red shift is naturally explained by the competition of the absorption bleaching and induced absorption effects: weaker absorption bleaching outweighs the induced absorption in a narrower spectral region. The dip at 2.1 eV in the induced absorption spectrum obtained at the initial time after excitation is an exceptional feature of this sample. Its position coincides with the weak additional band in the steady-state absorption spectrum, which is most likely caused by additional intraband defect level formed during the sample synthesis. Bleaching of this band partly compensates the induced absorption. Transient absorption kinetics is very similar to that observed in Sample 1 with the

major difference in the ratio of contributions of the fast and slow relaxation components. The slow relaxation is notably more expressed and it contributes about 30–40% to the total relaxation. Evidently smaller fraction of created conduction carriers relax through lower density of recombination centres forming deep middle-gap states.

Differential absorption data of as-deposited 48 nm diameter nanowires of nearly pure  $\text{Cu}_3\text{Se}_2$  (Sample 4) are presented in Fig. 5. Two bleaching bands with the maximum peak positions close to 1.3 and 1.7 eV are clearly observed in the transient absorption spectrum at the initial time after excitation. The bleaching bands are slightly blue shifted compared to the stationary absorption bands. Sample 4 shows no induced absorption in the investigated spectral range; bleaching of the two strong absorption bands dominates over the free carrier absorption. The slow relaxation component is almost absent in these samples. Evidently nearly all created carriers relax during several picoseconds through the high density of interband recombination states.

Peculiarities of transient absorption relaxation processes in a mixed stoichiometric copper selenide phase sample can be explained by an internal disorder and high density of various defects forming intraband recombination centres. Additional absorption bands created by the mid-gap defect states are effectively bleached under the sample excitation independently of the excitation photon energy. These states also cause fast transient absorption relaxation as there is a clear correlation between the intensity of the additional absorption bands and the relative contribution of the fast relaxation component.

#### 4. Conclusions

Investigation of nonlinear optical effects in copper selenide nanowires demonstrates a strong bleaching of the middle-gap states absorption band on the near-infrared side, whereas an induced absorption dominates in the visible light spectral range in annealed nonstoichiometric copper selenide samples. Relaxation of induced absorbance changes is described by two processes—fast relaxation during initial several picoseconds followed by a slower component with the characteristic relaxation time constant of a few tens of picoseconds. The initial relaxation is more expressed in an as-deposited sample of nearly pure  $\text{Cu}_3\text{Se}_2$  nanowires.  $\text{Cu}_3\text{Se}_2$  phase leads to the formation of additional middle-gap states resulting in the rise of absorption

bleaching in the visible spectral range. Higher concentration of the middle-gap states leads to more efficient ultrafast transient absorption relaxation of temporal optical features. The ability to adjust nonlinear optical properties of copper selenide nanowires is very attractive for their application. As-formed and nonannealed copper selenide nanostructures might be of a particular interest for fabrication of nonlinear optical elements that require fast optical response and nearly complete absorption bleaching recovery. Annealed samples with lower density of defects and local states can be used for devices that require longer lifetimes of nonequilibrium carriers.

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## SKIRTINGOS STECHIOMETRIJOS VARIO SELENIDO NANOVIELŲ NENUOSTOVIOJI SUGERTIS

G. Juška<sup>a</sup>, V. Gulbinas<sup>a</sup>, A. Jagminas<sup>b</sup>

<sup>a</sup> *Fizinių ir technologijos mokslų centro Fizikos institutas, Vilnius, Lietuva*

<sup>b</sup> *Fizinių ir technologijos mokslų centro Chemijos institutas, Vilnius, Lietuva*

### Santrauka

Vario selenidas – puslaidininkinė medžiaga, kurios įvairioms stechiometrinėms formoms būdingos savitos optinės savybės. Išskirtinė vario selenido nanostruktūrų savybė, lyginant su tūriniu kristalu, – papildoma homogeniškai išplitusi sugerties juosta, turinti maksimumą ties 1,2 eV. Tyrimo objektas – porėtame aliuminio oksido sluoksnyje elektrochemiškai nusodinto vario selenido nanovielų, dėl skirtingų sintezės ir apdorojimo parametrų (srovės tankio, rūgštingumo, atkaitinimo temperatūros) besiskiriančių optinėmis savybėmis, stechiometrija (nuo beveik grynos  $\text{Cu}_3\text{Se}_2$  iki nestechiometrinės  $\text{Cu}_{2-x}\text{Se}$  fazės). Šių nanostruktūrų nenuostoviosios sugerties savybės 1,2–2,88 eV intervale tirtos femtosekundi-

nės laikinės skyros sugerties žadinimo zondavimo metodika. Tyrimas rodo, kad visais atvejais nestechiometriniam  $\text{Cu}_{2-x}\text{Se}$  priskiriamai sugerties juostai artimojoje infraraudonoje srityje būdingas stiprus sugerties praskaidrėjimas, kuris atsistato po dviejų relaksacinių vyksmų – spartaus, pikosekundžių trukmės, ir lėtesnio, trunkančio kelis šimtus pikosekundžių. Regimosios šviesos srityje dominuoja indukuota sugertis, kurios relaksacijos trukmė analogiška. Bandiniuose su  $\text{Cu}_3\text{Se}_2$  faze beveik visi indukuoti sugerties pokyčiai atsistato per pirmąsias pikosekundes. Tokia kontroliuojamų optinių savybių įvairovė gali būti pritaikyta gaminant netiesinės optikos elementus.