The investigation of the kinetics of the losses of nonequilibrium current carriers in $Cu_{2-\delta}NiSnS_4$ ($0 \leq \delta \leq 0.2$) quaternary copper compounds

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By solid-phase synthesis from elemental Cu, Ni, Sn, and S samples $Cu_{2-\delta}NiSnS_4$ ($0 \leq \delta \leq 0.2$) was prepared. The parameters of their crystal lattice have been refined. The lifetimes of photogenerated current carriers in $Cu_{2-\delta}NiSnS_4$ were estimated for the first time by the contactless time-resolved microwave photoconductivity method. This times turned out to be $\tau \approx 7$ ns, which is comparable with the literature data for the times in kesterites CZTS. Herewith, in kinetics of loses of photogenerated cureent carriers is observed predominance of bimolecular recombination processes over capture processes.

Keywords: $Cu_{2-\delta}NiSnS_4$, onequilibrium current carriers, lifetimes, kinetics.

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1. Introduction

Various new types of energy sources, of which photovoltaic converters are an example, are now being used more and more widely. Quaternary copper compounds with the $Cu_{2-\delta}ZnSnS_{4-y}Se_y$ (CZTS(Se)) kesterite structure appear to be promising materials for the fabrication of such converters. However, the efficiency of solar cells based on them still remains below 13%, which is far from the theoretical Shockley–Queisser limit ($\sim 30\%$) [1]. Apparently, this is attributable to the material structure. It is assumed that, due to the similarity of ionic radii of Zn^{2+} and Cu^{+}, a great number of antisite defects Cu_{Zn} and Zn_{Cu} form in such a material and act as carrier traps [2,3]. Therefore, the substitution of ions in the cation sublattice of this material with ions with a radius differing from the one for Cu^{+} is of considerable academic and practical interest.

Among such materials are quaternary copper compounds with the $Cu_{2-\delta}NiSnS_4$ (CNTS) general formula [4,5]. The lifetime of photogenerated carriers in a semiconductor is one of the factors governing the efficiency of a solar cell.

The time-resolved luminescence technique [6], which is based on the examination of decay kinetics of the emission spectrum, is the most widely used method for probing the kinetics of photogenerated carrier loss. However, this method is applicable only to processes involving light emission (e.g., recombination luminescence). It is not suitable for the detection of nonradiative processes of free carrier loss: capture by acceptors and traps, electron–hole recombination, and recombination via localized states (including the case of nonradiative luminescence). Electrical methods are more broadly applicable.

The frequency- and time-resolved microwave photoconductivity technique belongs to this class of methods [7,8]. In the present study, the contactless microwave photoconductivity method was used to examine the influence of copper concentration on the kinetics of non-equilibrium carrier loss in $Cu_{2-\delta}NiSnS_4$ ($0 \leq \delta \leq 0.2$) compounds produced by solid-phase ampule synthesis.

2. Experimental

Samples for experiments were prepared by direct synthesis from elemental copper (4N), nickel (3N), tin (4N), and sulfur (ACS). Synthesis was performed in evacuated (residual pressure $p = 10^{-2}$ mm Hg) carbonized quartz ampules in several stages. At the first stage, NiS and the $Cu_{2-\delta}SnS_3$ ternary compound were produced from the corresponding elements. Synthesis was carried out at $T = 1100^{\circ}$C within 10 h. Following cooling, the ampule contents were ground in agate mortars for homogenization, sealed up again in vacuum, and annealed at $T = 740^{\circ}$C for 48 h. At the next stage, the needed amounts of NiS and $Cu_{2-\delta}SnS_3$ were introduced into an evacuated quartz ampule and annealed at $T = 1100^{\circ}$C for 10 h. The last stage involved grinding the obtained ingots in agate mortars, sealing them in an ampule in vacuum, and annealing at $T = 520^{\circ}$C for 600 h.

X-ray diffraction analysis (XRD) was performed to determine the structure of the synthesized samples using a „PANalitical Aeris diffractometer" (CuK_α radiation) provided by the Analytical Common Use Center of the Institute of Problems of Chemical Physics of the Russian Academy of Sciences. The phase composition was identified using the ICDD XPDF-4+2020 electronic crystallographic database. Diffraction patterns were processed in WinXPOW. The phase composition was studied additionally by Raman spectroscopy („Bruker Senterra micro-Raman System", 532 nm radiation).

The method of room-temperature time-resolved microwave photoconductivity in the frequency range of 36 GHz („Setup for Measurement of Lifetimes of Photogenerated Carriers by the Microwave Photoconductivity Method in the Frequency Range of 36 GHz") was used to examine the kinetics of photogenerated carrier loss. The temporal resolution of the detection circuit was ~ 5 ns [7,8]. Photoconductivity was excited by an LGI-21 nitrogen laser with emission wavelength $\lambda = 337$ nm and a pulse duration of 8 ns. The maximum luminous flux density incident on a sample in a single pulse (exposure) was 10^{15} photon/cm^2. The light intensity in experiments was adjusted with the use of light filters.

3. Results and discussion

Figure 1 shows the X-ray diffraction data for the synthesized samples.

It can be seen that all the higher-intensity lines correspond to the primary phase, $Cu_{2-\delta}NiSnS_4$ (ICDD PDF-4+2020, card №. 00-026-0552). The structure is cubic, and the space group is $F-43$ m. The revised parameters of the crystal lattice are as follows: $a = 5.41$ Å, $V = 161.4$ Å^3 for Cu_2NiSnS_4, $a = 5.45$ Å, $V = 161.8$ Å^3 for $Cu_{1.9}NiSnS_4$, $a = 5.45$ Å, $V = 161.9$ Å^3 for $Cu_{1.8}NiSnS_4$.

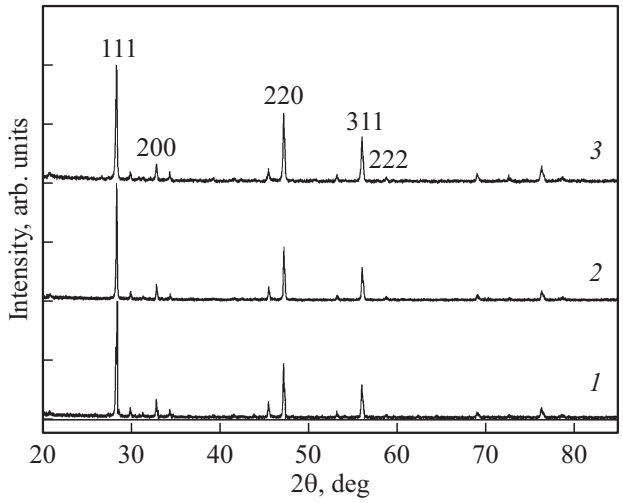

Figure 1. XDA data for $Cu_{2-\delta}NiSnS_4$ samples: $\delta = 0$ (*1*), 0.1 (*2*), 0.2 (*3*).

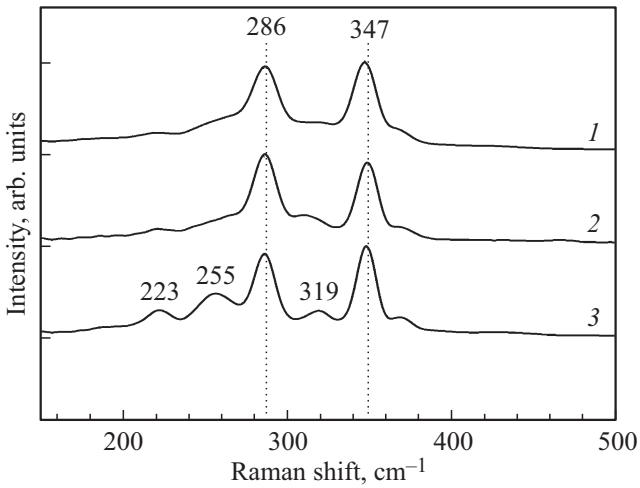

Figure 2. Raman spectroscopy data for $Cu_{2-\delta}NiSnS_4$ samples: $\delta = 0$ (*1*), 0.1 (*2*), 0.2 (*3*).

Figure 2 shows the Raman spectra of the synthesized samples.

Literature data on the positions of peaks in Raman spectra are contradictory [9–11]. The positions of the most intense peaks in the measured Raman spectra (347 and 286 cm^{-1}) are close to those given in [10]. Therefore, these lines should belong to the primary phase (CNTS). In the samples with $\delta = 0.2$, the lines of impurity phases (223, 255, 319 cm^{-1}) are observed alongside with those typical of CNTS. These impurity phases are likely to be copper sulfides (Cu_2SnS_3 or $Cu_2NiSn_3S_8$).

The results of examination of the kinetics of photogenerated carrier loss revealed that when the light was switched on, the reflected power first increased sharply (photoresponse) and then returned gradually to the initial state. Having analyzed the entire set of experimental data, we found that the rate of photoresponse decay was fairly high; thus, it proved difficult to determine the shape of curve dips. The microwave photoconductivity drops for Cu_2NiSnS_4 and $Cu_{1.9}NiSnS_4$ powders are shown in Fig. 3 for illustrative purposes. It can be seen that the photoresponse amplitudes differ approximately by a factor of 2, and the calculated decay times are 7 ns (limited by the temporal resolution of the setup).

The $\Delta P_{\max}(I)$ dependences were nonlinear for almost all samples (Fig. 4 illustrates this), and the characteristic decay time did not depend on incident light intensity I. This suggests that processes of the second reaction order (recombination of free electrons and holes) transpired in experiments within < 5 ns:

$$e^- + p^+ \xrightarrow{k_{\text{rec}}} \dots . \qquad (1)$$

However, the initial section of $\Delta P_{\max}(I)$ remains linear up to $I = 3 \cdot 10^{14}$ photon $\cdot$ cm^{-2} per pulse. This suggests that

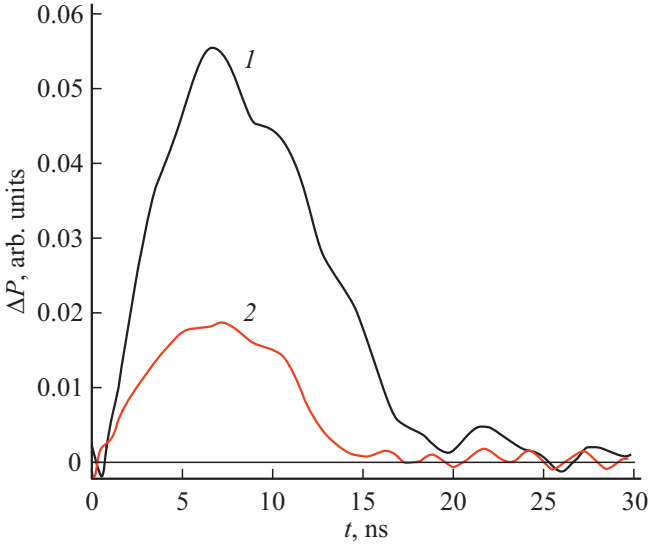

Figure 3. Microwave photoconductivity decay for Cu_2NiSnS_4 (*1*) and $Cu_{1.9}NiSnS_4$ (*2*) powders. $I = 8.7 \cdot 10^{14}$ photon $\cdot$ cm^{-2} per pulse. The curves were smoothed over 7 points using a linear filter.

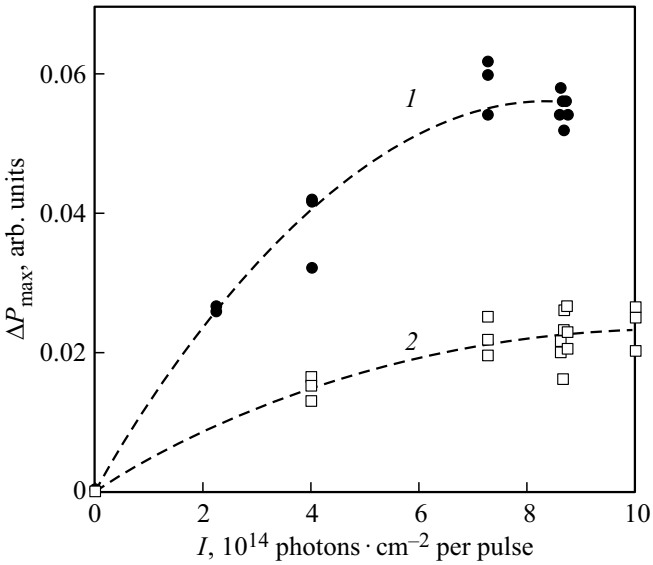

Figure 4. Dependences of the photoresponse amplitude on the incident light intensity for Cu_2NiSnS_4 (*1*) and $Cu_{1.9}NiSnS_4$ (*2*) powders.

the first-order process (capture of carriers by traps) is prevalent at incident light intensities $< 3 \cdot 10^{14}$ photon $\cdot$ cm^{-2} per pulse:

$$e^- + A \xrightarrow{1/\tau_{tr}^e} A^-, \quad (2)$$

$$p^+ + B \xrightarrow{1/\tau_{tr}^p} B^+, \quad (3)$$

where τ_{tr}^e and τ_{tr}^p are the lifetimes to capture of electrons and holes, respectively. The following relation then holds true for $I = 3 \cdot 10^{14}$ photon $\cdot$ cm^{-2} per pulse: $\tau_{tr}^e = \tau_{rec} = 1/k_{rec}k_B\beta I$, where k_{rec} is the electron–hole recombination rate constant, k_B is the absorption coefficient, and β is the quantum yield. The lifetimes of carriers may then be estimated. If we assume that, in accordance with [10], $k_{rec} \sim 10^{-10}$ cm$^3 \cdot$ s^{-1} for a bandgap width of 1.2 eV [9] and $k_B = 10^6$ cm^{-1} [11], lifetime $\tau_{tr}^e \approx 0.03$ ns. It is evident that the calculated time to capture of carriers is approximately 2 orders of magnitude shorter than the measured characteristic time of photoresponse decay. This may indicate that the so-called „secondary" processes driven by processes (4)–(6) are observed instead of carrier capture in experiments:

$$p^+ + A^- \xrightarrow{1/\tau_{rec}} A, \quad (4)$$

$$A^- \xrightarrow{1/\tau^e} e^- + A, \quad (5)$$

$$B^+ \xrightarrow{1/\tau^p} p^+ + B, \quad (6)$$

where τ_{rec} is the lifetime to recombination of localized electrons and free holes (recombination via local centers) and τ^e and τ^p are the times of thermal release of captured carriers from electron (A) and hole (B) traps, respectively.

Thus, the estimated lifetimes to capture of photogenerated carriers in $Cu_{2-\delta}NiSnS_4$ turned out to be shorter than the lifetimes for polycrystalline CZTS kesterites determined in our earlier microwave photoconductivity studies [11] and measured by the authors of [12] with the use of the time-resolved luminescence method. However, the lifetimes of carriers released back from traps are ~ 7 ns and are comparable with literature data.

4. Conclusion

Thus, $Cu_{2-\delta}NiSnS_4$ ($0 \le \delta \le 0.2$) samples were synthesized by solid-phase synthesis from elemental Cu, Ni, Sn, and S. Their structure and parameters of their crystal lattice were determined by XRD and Raman spectroscopy. The kinetics of photogenerated carrier loss in $Cu_{2-\delta}NiSnS_4$ powders was examined for the first time using the contactless time-resolved microwave photoconductivity method. It was demonstrated that the processes of electron–hole recombination dominate over carrier capture processes at incident light intensities $> 3 \cdot 10^{14}$ photon $\cdot$ cm^{-2} per pulse. The measured lifetimes of photogenerated carriers ($\tau \approx 7$ ns) were considerably longer than the lifetimes to capture (~ 0.03 ns) estimated based on the bandgap width of CNTS. This is apparently attributable to secondary processes.

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The unique „Setup for Measurement of Lifetimes of Photogenerated Carriers by the Microwave Photoconductivity Method in the Frequency Range of 36 GHz" and other equipment provided by the Analytical Common Use Center of the Institute of Problems of Chemical Physics of the Russian Academy of Sciences was used in the study, which was conducted under state assignment No. AAAA-A19-119070790003-7.

Conflict of interest

The authors declare that they have no conflict of interest.

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