

OPTICAL INVESTIGATION AND APPLICATION OF COPPER SELENIDE NANOWIRES *

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Growth and optical properties of copper selenide nanowires (nws) in alumina template were studied and discussed in respect to their application as films doped with semiconductor nanocrystals that provide promising optical properties. The results obtained indicate that nanoscaled copper selenide structures uniformly embedded at the bottom of alumina less than a micron in depth could be useful for mode locking in picosecond YAG type lasers. The operating wavelength of the material was identified by optical characterization. Copper selenide nanowires were examined as saturable absorber to yield passive wave mode-locking in a Nd³⁺/YAG laser ($\lambda = 1.064 \mu\text{m}$). Both the deposition conditions and subsequent annealing define the stoichiometry of copper selenides providing a slight shift of absorption spectra.

Keywords: copper selenide nanowires, picosecond YAG laser, mode-locking

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One of the preponderant modern sciences nowadays is nanotechnology. While studying new semiconductor nanomaterials, great interest arrived for copper selenide nanoparticles [1–9]. One of their promising applications is optical switching devices, because of the transient bleaching effect [7–9]. Size, chemical composition, and crystalline structure of nanoparticles determine the character of light absorption processes – same as for indirect *p*-type semiconductor, copper selenide Cu_{*x*}Se_{*y*}. Under ambient conditions the material exists as a series of stable and metastable phases, with the stoichiometry coefficients *x* and *y* varying from 1 to 3. Variation in stoichiometry results in change of crystalline structure, absorption spectra, and both direct and indirect band gap $E_{g,\text{dir}}$, $E_{g,\text{indir}}$ values [10]. Moreover, the crystalline structure and phase composition of copper selenide leads to different optical and other properties obtainable by annealing of specimens.

In recent years, a number of researchers have explored semiconductor nanocrystals as saturable absorbers to create passive mode-locked solid-state lasers [7–9]. Nanostructured copper selenide appears to gain shallow absorption centres characterized by the absorp-

tion peak in near-IR, which leads to optical nonlinearity effects [10]. The observed absorption range appears to be consistent with the first harmonic of YAG type solid state laser (wavelength within 1–1.5 μm).

We studied here for the first time the nonlinear optical properties and mode-locking performance of porous alumina thin films containing copper selenide. Thus, arrays of nanoscaled Cu₃Se₂ (umangite) before and after annealing at several different temperatures were fabricated and investigated.

Aluminium foil of 100 μm in thickness and 99.995 at% purity from Goodfellow was used to prepare samples of $12 \times 12.5 \text{ mm}^2$ in dimensions. Before anodizing, the surface of samples was cleaned by degreasing in acetone, etching in a hot 1.5 M NaOH solution for 20 s, desmutting in 10% HNO₃, thoroughly rinsing, and drying in nitrogen stream. The growth of porous aluminium oxide was performed by direct current (dc) anodizing of cleaned samples in a stirred solution of 0.3 M oxalic acid at 17 °C and 40 V for 45 min using two coal stripes as cathodes.

Electrodeposition of copper selenides within the alumina pores was performed in a glass cell in which two graphite rods were used as the auxiliary and an Al/alumina as working electrodes. The solution

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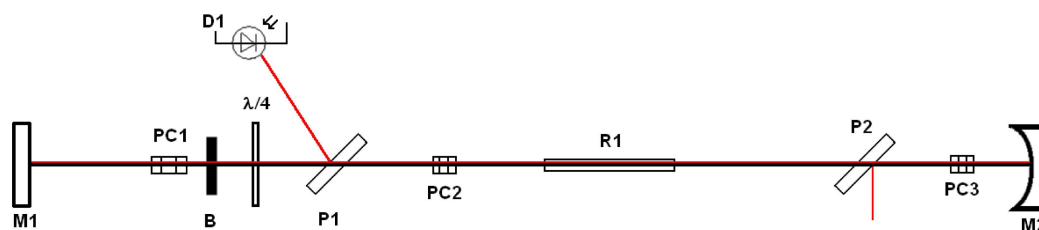


Fig. 1. Schematic view of picosecond $\text{Nd}^{3+}:\text{YAG}$ laser resonator: $R1$ is active media, B is investigated sample, $D1$ is photodiode, $P1$ and $P2$ are polarizers, $M1$ and $M2$ are back mirrors, $PC1$, $PC2$, and $PC3$ are Pockels elements.

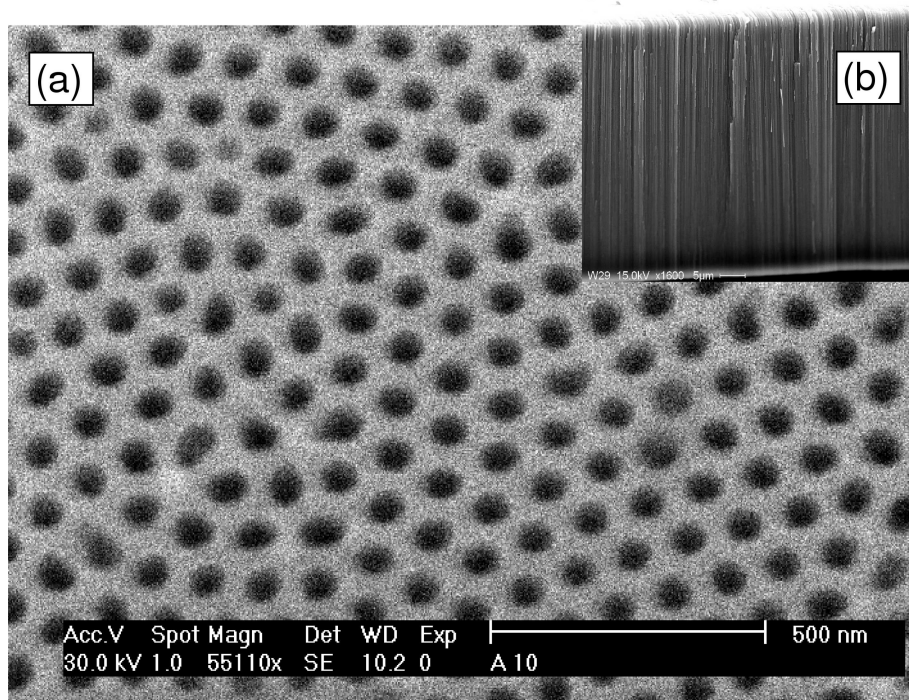


Fig. 2. SEM micrographs of aluminium oxide columns: (a) top view, (b) side view.

containing CuSO_4 , H_2SeO_3 , and MgSO_4 as in earlier study [11] kept at room temperature was used to deposit almost pure phase of Cu_3Se_2 . The proper acidity of solution was adjusted by H_2SO_4 . The deposition of copper selenide was carried out using the alternating current (ac), 50 Hz in frequency, centring at 0 V, under constant ac current density (j_{ac}) mode of $\sim 4.0 \text{ mA/cm}^2$ for 1 to 30 min. The solution was stirred during deposition.

The annealing of samples was carried out in an open oven at 100, 150, 200, 300, 350, and 400 °C temperatures for an hour.

X-ray diffraction measurements were performed with a diffractometer D8 (Bruker AXS, Germany) equipped with a Göbel mirror using $\text{Cu K}\alpha$ radiation and step-scan mode with a step magnitude of 0.02° and a counting time of 20 s in the 2θ range from 15 to 55° .

The optical absorption spectra of copper selenide arrays within the alumina pores was determined from

transmittance spectra recorded in respect to pure alumina matrix using spectrophotometer Shimadzu UV-3101PC.

Picosecond $\text{Nd}^{3+}:\text{YAG}$ laser resonator was used to verify the relevance of aluminium oxide thin films containing copper selenide nanowires for laser light mode-locking. Schematic view of the laser resonator used is presented in Fig. 1.

Scanning electron microscopy (SEM, Philips XL model) conventional analysis showed the densely positioned aluminium oxide columns each containing a nanochannel inside (see Fig. 2(a,b)). Via additional etching in 0.5 M phosphoric acid solution at 30 °C for 30 min, widening of alumina channels was performed. Templates containing cells of about 108 nm in size and nanochannels close to 45 nm in diameter and about $7 \mu\text{m}$ long were fabricated.

The XRD patterns of samples annealed at different temperatures are presented in Fig. 3. Stoichiometric

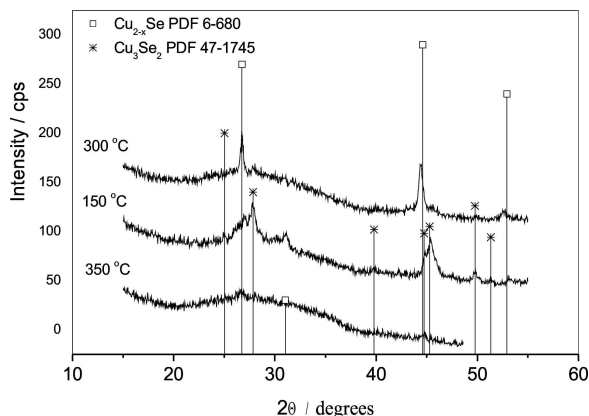


Fig. 3. X-ray diffractogram for copper selenide nanowires annealed at different temperatures (150, 300, and 350 °C).

Cu_3Se_2 consists of metastable phase of copper selenide that changes structure at higher temperatures. Experiments prove that annealing at 150 °C and higher temperatures leads to restructuring of Cu_3Se_2 to non-stoichiometric Cu_{2-x}Se phase. Parameter x tends to decline upon rising temperature. The crystal size increases and the energy band gap declines when x approaches zero [12–18]. As expected, the change of crystalline structure after annealing of stoichiometric Cu_3Se_2 compound was observed. This effect is possibly determined by diffusion of selenium from the compound. The sample annealed at 150 °C is mainly a two-phase composition of stoichiometric Cu_3Se_2 and non-stoichiometric Cu_{2-x}Se phase. Typical XRD pattern of the sample annealed at 350 °C did not show any crystalline phase of copper, selenium, or copper selenides. Sample annealed at 400 °C did not show any phase either. However, annealing at 300 °C provided homogeneous $\text{Cu}_{1.85}\text{Se}$ phase.

Figure 4 shows absorption spectrum for the annealed alumina samples containing copper selenide nanowires (100, 200, 300, 400 °C). All the samples possess strong absorption peak close to 1 eV, however, the position of the peak slightly varies from sample to sample. Rise of the annealing temperature diminishes the absorption coefficient value. This effect is determined by compositional changes during the annealing process. A slight shift of the absorption peak was observed as well: a red shift with annealing temperature.

Testing the samples within Nd^{3+} : YAG laser resonator, indication of mode-locking was observed (see oscillogram in Fig. 5). Sample annealed at 300 °C tends to indicate mode-locking. However, the as-deposited sample and those annealed at 100, 150, 200, 350, and 400 °C temperature showed poor or even no effect in that case. After testing the 300 °C sample vi-

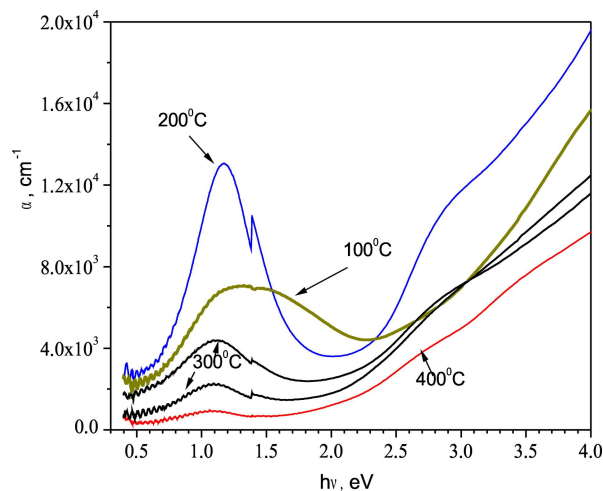


Fig. 4. Absorption spectra of samples annealed at different temperatures (100, 200, 300, and 400 °C). At 300 °C upper (lower) curve obtained before (after) laser irradiation (see text for explanation).

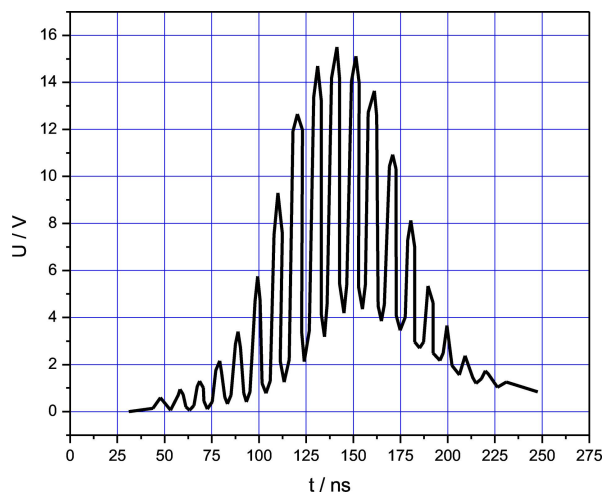


Fig. 5. Mode-locked signal obtained using copper selenide nanowires as saturable absorber (oscillograph Tektronix TDS-220).

sual change of sample colour (a track) was observed. It seems that the effect arises only after laser light has been applied. Absorption analysis of the laser-affected sample did not show discernible absorption shift, only a slight reduction of absorption (see Fig. 4).

In conclusion, aluminium oxide matrixes with copper selenide nanowires of different phase inside were fabricated. Investigation of structural and optical properties of copper selenide nanowires, together with a test of samples as saturable absorber in Nd^{3+} : YAG laser for mode-locking at 1.064 μm wavelength, was performed. It was found that $\text{Cu}_{1.85}\text{Se}$ fits best for this laser application.

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References

- [1] S. Xu, H. Wang, J.-J. Zhu, and H.-Y. Chen, *J. Cryst. Growth* **234**, 263–266 (2002).
- [2] H.-L. Li, Y.-C. Zhu, S. Avivi, O. Palchik, J.-P. Xiong, Y. Koltypin, V. Palchik, and A. Gedanken, *J. Mater. Chem.* **12**, 3723–3727 (2002).
- [3] H. Su, Y. Xie, B. Li, and Y. Qian, *Mater. Res. Bulletin* **35**, 465–469 (2000).
- [4] M.A. Malik, P. O’Brien, and N. Revaprasadu, *Adv. Mater.* **11**, 1441–1444 (1999).
- [5] Y. Zhang, Z.-P. Qiao, and X.-M. Chen, *J. Mater. Chem.* **12**, 2747–2748 (2002).
- [6] X. Changqi, Z. Zhicheng, Y. Qiang, and Z. Guixi, *Mater. Res. Innovat.* **8**, 166–167 (2004).
- [7] K.V. Yumashev, N.N. Posnov, I.A. Denisov, V.P. Michailov, and P.V. Prokoshin, *J. Opt. Soc. Am. B* **7**, 572–579 (2000).
- [8] S.A. Zolotovskaya, N.N. Posnov, P.V. Prokoshin, K.V. Yumashev, V.S. Gurin, and A.A. Alexenko, *Semicond.* **38**, 812–817 (2004).
- [9] S.A. Zolotovskaya, V.G. Savitski, P.V. Prokoshin, and K.V. Yumashev, *J. Opt. Soc. Am. B* **23**, 1268–1275 (2004).
- [10] e.g. G. Statkutė, R. Tomašiūnas, and A. Jagminas, *J. Appl. Phys.* **101**, 113715–1–9 (2007).
- [11] A. Jagminas, R. Juškėnas, I. Gailiūtė, G. Statkutė, and R. Tomašiūnas, *J. Cryst. Growth* **294**, 343–348 (2006).
- [12] A.S. Povarennykh, *Crystal Chemical Classification of Minerals* (Plenum Press, New York, 1972).
- [13] M.A. Korzhuev, V.Yu. Fedotov, N.Kh. Abrikosov, and V.F. Bankina, *Sov. Phys. Solid State*, **27**, 2189 (1984).
- [14] K.V. Yumashev, V.S. Gurin, P.V. Prokoshin, V.B. Prokopenko, and A.A. Alexenko, *Phys. Status Solidi* **224**, 815 (2001).
- [15] B. Pejova and I. Grozdanov, *J. Solid State Chem.* **158**, 49–54 (2001).
- [16] D. Lippkow and H.H. Strehblow, *Electrochimica Acta* **43**, 2131 (1998).
- [17] S.R. Gosavi, N.G. Deshpande, Y.G. Gudage, and R. Sharma, *J. Alloys Compounds* (2007) [corrected proof available online].
- [18] V.M. Garcia, P.K. Nair, and M.T.S. Nair, *J. Cryst. Growth* **203**, 113 (1999).

VARIO SELENIDO NANOVIELŲ OPTINIS TYRIMAS IR TAIKYMAS

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Santrauka

Puslaidininkiniais nanodariniiais – vario selenido nanovielomis – susidomėta po to, kai jų optiniame spektre ties 1 μm bangos ilgiu buvo pastebėtas rezonansinis sugerties maksimumas. Taigi, atsirado nauja nanodarinių medžiaga, perspektyvi taikymams netiesinėje optikoje. Šiuolaikinės anodavimo technologijos leidžia pagaminti nanometrų eilės ertmės aliuminio okside, į kurias elektrochemiškai gali būti nusodintos įvairios medžiagos, tame tarpe ir vario selenidas. Aptariama vario selenido nanovielų formavimo technologija, pateikiami eksperimentiniai nanovielų sandaros ir optinių

savybių tyrimų bei taikymo lazerio spinduliuotės modų sinchronizacijai rezultatai. Tyrimai parodė, kad vario selenido nanovielas įmanoma panaudoti pikosekundiniuose YAG tipo lazeriuose modų sinchronizacijai. Nustatyta, kad gautų vario selenido nanodarinių sugerties juosta yra ties pagrindine Nd^{3+} / YAG lazerio bangos ilgio verte $\sim 1,064 \mu\text{m}$. Eksperimentų metu taip pat pastebėta, kad, keičiant medžiagų santykinę atomų sudėtį, keičiasi ir darinių parametrai: kristalinė sandara, sugerties spektras. Tokiu būdu atsivertų galimybės šiuos darinius taikyti lazeriams ir su kitos rūšies aktyviosiomis terpėmis.