## 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 Nd<sup>3+</sup> / YAG laser ( $\lambda = 1.064 \ \mu m$ ). 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  $E_{g,dir}$ ,  $E_{g,indir}$  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 absorption 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  $\mu$ m).

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  $Cu_3Se_2$  (umangite) before and after annealing at several different temperatures were fabricated and investigated.

Aluminium foil of 100  $\mu$ m in thickness and 99.995 at% purity from Goodfellow was used to prepare samples of 12 × 12.5 mm<sup>2</sup> 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% HNO<sub>3</sub>, 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

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Fig. 1. Schematic view of picosecond  $Nd^{3+}$ : 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.

Al/alumina as working electrodes. The solution contain CuSO<sub>4</sub>, H<sub>2</sub>SeO<sub>3</sub>, and MgSO<sub>4</sub> as in earlier study [11] kept at room temperature was used to deposit almost pure phase of Cu<sub>3</sub>Se<sub>2</sub>. The proper acidity of solution was adjusted by H<sub>2</sub>SO<sub>4</sub>. 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 ~4.0 mA/cm<sup>2</sup> 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  $^{\circ}$ C temperatures for an hour.

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

The optical absorption spectra of copper selenide

Picosecond Nd<sup>3+</sup> : 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  $\mu$ m long were fabricated.



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

The XRD patterns of samples annealed at different temperatures are presented in Fig. 3. Stoichiometric Cu<sub>3</sub>Se<sub>2</sub> 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<sub>3</sub>Se<sub>2</sub> to nonstoichiometric  $Cu_{2-x}$ 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 twophase composition of stoichiometric Cu<sub>3</sub>Se<sub>2</sub> and nonstoichiometric  $Cu_{2-x}$ 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  $Cu_{1.85}$ 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



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).

 $400 \,^{\circ}\text{C}$  temperature showed poor or even no effect in that case. After testing the 300  $^{\circ}\text{C}$  sample visual 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<sup>3+</sup> : YAG laser for mode-locking at 1.064  $\mu$ m wavelength, was performed. It was found that Cu<sub>1.85</sub>Se fits best for this laser application.

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#### References

- 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. Prokosin, J. Opt. Soc.

Am. B 7, 572–579 (2000).

- [8] S.A. Zolotovskaya, N.N. Posnov, P.V. Prokosin, K.V. Yumashev, V.S. Gurin, and A.A. Alexenko, Semicond. 38, 812–817 (2004).
- [9] S.A. Zolotovskaya, V.G. Savitski, P.V. Prokosin, 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 nanodariniais – vario selenido nanovielomis – susidomėta po to, kai jų optiniame spektre ties 1  $\mu$ m bangos ilgiu buvo pastebėtas rezonansinis sugerties maksimumas. Taigi, atsirado nauja nanodarinių medžiaga, perspektyvi taikymams netiesinėje optikoje. Šiuolaikinės anodavimo technologijos leidžia pagaminti nanometrų eilės ertmes 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<sup>3+</sup> / YAG lazerio bangos ilgio verte ~1,064  $\mu$ 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.