ISSN 1560-8034, 1605-6582 (On-line), SPQEO, 2019. V. 22, N 2. P. 231-236.

Luminescent analysis of the quality of CdS nanocrystals depending on technological parameters

A.B. Bogoslovskaya, D.O. Grynko, E.G. Bortchagovsky, O.I. Gudymenko

V. Lashkaryov Institute of Semiconductor Physics of NAS of Ukraine,
41, prospect Nauky, 03680 Kyiv, Ukraine,
E-mail: bogoslovskaya@ukr.net

Abstract. This work is devoted to luminescent investigations of CdS nanowhiskers grown in different technological approaches with variable parameters, allowing to control sizes and morphology of grown nanocrystals. Luminescence was used for the express analysis of the influence of technological parameters on the quality of grown crystals by comparison of band-edge and defect luminescent bands.

https://doi.org/10.15407/spqeo22.02.231
PACS 68.70.+w, 71.55.Gs, 78.55.-m

Keywords: CdS, whiskers, photoluminescence, crystal morphology.

Manuscript received 23.04.19; revised version received 13.05.19; accepted for publication 19.06.19; published online 27.06.19.

1. Introduction

Last decades demonstrate rocket growth of the interest to nanostructured materials. It is explained both by unique properties on nanomaterials as compared to their bulk form and by the possibility to tune in easy way their size-dependent properties in a wide range [1-3]. The latter outcomes in growing application of nanomaterials in electronics, sensorics, materials science, energetics and many other fields, which goes along the demand of further miniaturization and decreasing energy consumption in modern devices. One direction in the construction of functional nanodevices based on the one-dimensional semiconductor materials combines advances of nanomaterials and integration of these elements with other circuits without additional contacts. Nanodevices, such as transistors [4], light emission diodes (LED) [5], laser [6], photodetectors [7], gas and chemical sensors [8-10], solar cells [11], *etc*., have been reported as demonstrating exciting progress in the "bottom-up" approach for building new-generation electronic and photoelectronic systems with reduced sizes, higher efficiency, and less energy consumption. However, important or even vital properties of these nanoelements are their crystallinity and defectness, which affects and can damage desired functions.

We grow nanowhiskers of cadmium sulfide by chemical condensation of CdS from the gas phase. CdS was chosen as promising semiconductor that has received considerable attention because of their intrinsic properties of a wide direct band gap (2.42 eV), high photosensitivity and good chemical stability [12-14]. It may be used in optoelectronics, and its piezoelectric properties enlarge the area of its possible application. To provide express controlling the influence of technological parameters on the quality of prepared crystals, we use luminescence at room temperature. So, the aim of this work is to discuss correlation of technological parameters and approaches with luminescent properties of grown CdS whiskers and their structure.

2. Experimental

Nanocrystals of CdS were grown using chemical condensation from the gas phase in a quasi-closed volume. This technique allows growing single crystals of cadmium sulfide with a diameter from tens to hundred nanometers and the length up to millimeters defined by the time of the growth. Crystals may be grown of both wurtzite and sphalerite type of symmetry. The scheme of the reactor is shown in Fig. 1.

The semi-closed volume is arranged in the silica cylindrical tube *1* with two end caps *2*. The reactor volume is pumped out with cryogenic sorption pump. The residual pressure is about 10^{-7} bar. Heating the reactor is carried out by seven heating sections *10* to *16* located outside of the tube in ambient atmosphere. The temperature of individual heating sections is stabilized independently by using a multi-channel thermostat. Substrates *6*, *7* are mounted on graphite pedestals *8*. The silica crucibles *3* and *4* are loaded with CdS and S ultra-high purity powder. The source *4* is equipped with additional resistive heater possessing small heat capacity for oversaturation control and stepwise change for 3…10 s.

© 2019, V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine

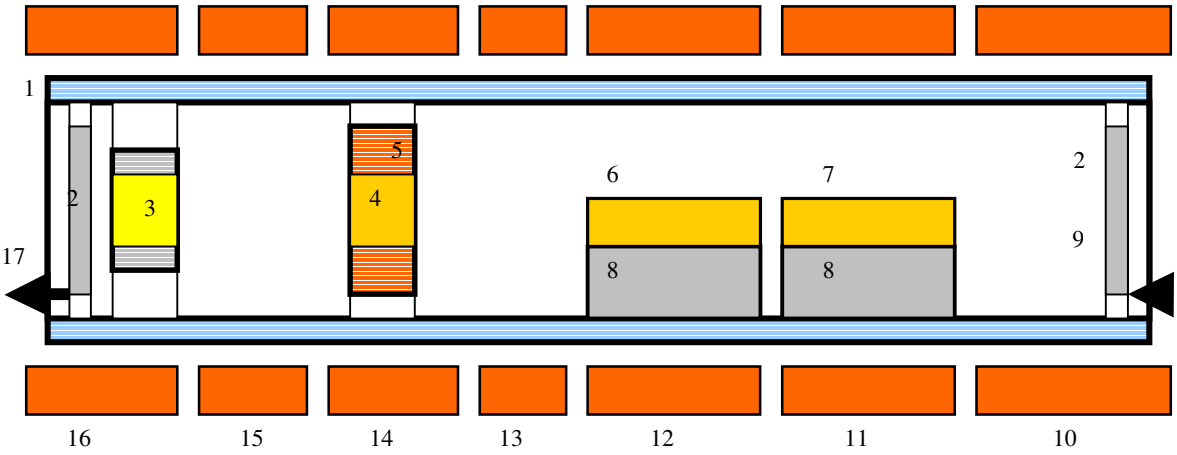


Fig. 1. Reactor for growing CdS nanocrystals: *1* – cylindrical silica tube, *2* – quasi-closed volume door, *3* – additional S vapor source, *4* – Cd and S vapor source with CdS powder, *5* – heater with small heat capacity, *6*, *7* – substrates with different temperatures, *8* – graphite stages, *9* – inlet valve, *10* to *16* – coaxial ceramic heaters, *17* – evacuation to cryogenic vacuum pump.

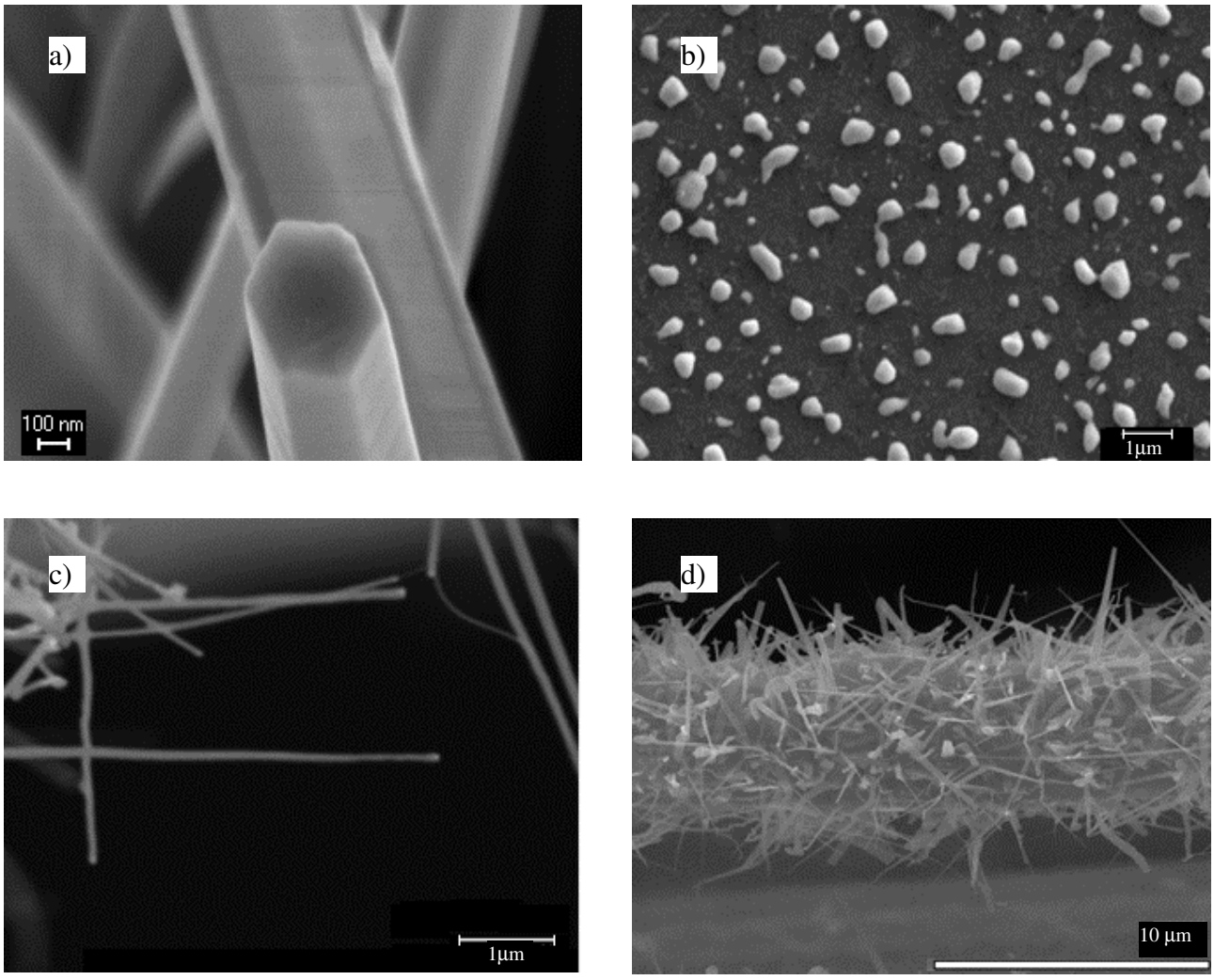


Fig. 2. Typical SEM images of CdS whiskers grown using the VS method (a), VLS method (c) and the micro-crucible one on a pyrolytic carbon fiber (d). Small gold droplets are visible on ends of whiskers (c). The panel (b) demonstrates the annealed gold film to realize the VLS growth.

Temperatures of the vapor sources *3* and *4* and substrate holders 8 are measured with miniature thermocouples. Molybdenum glass, glass covered by ITO film and fibers of pyrolytic carbon were used as substrates for crystal growth. The temperature of substrates was kept for the growth independently either at about 440…470 °C or about 620…670 °C.

The additional source of sulfur vapor *3* was used to obtain gaseous medium with an excessive content of sulfur contrary to stoichiometric concentration with respect to Cd. Thermodynamic calculations demonstrate that CdS crystal inevitably grows with sulfur vacancies, which can be partially compensated by sulfur oversaturation [15]. Additionally, annealing of CdS crystal in the atmosphere of sulfur vapor is the widely known method for compensating surface and bulk cadmium interstitial atoms. The temperature of the source *3* was 100…120 °C. CdS crystals were grown as well as annealed in this gaseous medium.

The crystals were grown using three different methods: vapor-solid (VS), vapor-liquid-source (VLS) [3, 16, 17] and micro-crucible. The crystals grow from the free end in the case of two first methods and from the bottom end in micro-crucible. In the case of clean surfaces, VS growth is realized when Cd and S vapors condensate on the free end of whiskers and chemically interact growing the crystal. In the VLS method some additional materials are used as nuclei and "catalyzer" of the crystal growth being situated in the form of liquid film on the free end of growing crystal [16]. In this case, the crystals grow on the solid-liquid interface. Crystals grow faster at VLS method in comparison to the VS one, and the size of nucleus defines the diameter of the whisker. However, despite it is assumed that those additional materials work as catalyzer with no inclusion into growing crystal as impurity, the question is not finally resolved. In our case, gold or silver was used for this growth. Initial nuclei were produced by vacuum deposition of thermally evaporated metals on the substrate to the mass thickness 0.5…2.5 nm and the following annealing of the substrate directly in vacuumed reactor by stepwise heating up to 500 °C for 1.5 hours. The growth by using the micro-crucible method was realized on fibers from pyrolytic carbon previously treated by thermo-chemical etching to produce well-developed surface with micro-crucibles [18]. Results of the growth of CdS whiskers by applying different methods are shown in Fig. 2.

Photoluminescence was studied at room temperature with the MDR-23 spectrometer and PMP-100 photomultiplier as a detector. The excitation source was semiconductor laser with the wavelength 407 nm. In addition, the samples were studied using scanning electron microscopy (SEM) that was performed with JEOL JSM35, JXA-8200. The phase composition of the films was analyzed by *ex-situ* X-ray diffraction carried out with a Philips X'Pert PRO X-ray diffractometer with CuKα radiation (λ = 0.154 nm). The qualitative phase analysis of the diffractogram was carried out using the ICDD database, PDF-2 Release 2012.

3. Results and discussions

All the spectra of photoluminescence have similar form – one band around 510 nm, which is prescribed to band-edge luminescence, and another wide band close to 670…710 nm, which is prescribed to luminescence of deep traps. There are many assumptions about the origin of this defect luminescence. It may be sulfur vacancies, cadmium interstitial atoms, surface states, *etc*. [12, 19-22]. Moreover, different hypotheses don't contradict to each other. Since all the measurements were made at room temperature, no fine structure at the band edge [23] is observed.

As the amount of CdS deposited on various surfaces is different, direct comparison of luminescence or absorption spectra is not possible. However, the ratio of the maximal intensity of the defect band to the band-edge luminescence may serve as an indicator of the quality of grown CdS whiskers. So, practically all shown spectra are normalized. The comparison of crystals grown using the VS and VLS methods is shown in Fig. 3.

Crystals, which luminescence is shown in Fig. 3, were grown at temperatures close to 450 °C. It is visible that the strongest relative band-edge luminescence is for CdS grown using the VS method – the ratio here is 2.2. The ratios for samples grown by VLS method are rather close: 9.9 for the sample 2, 7.3 for the sample 3 and 10.6 for the sample 4. The shown spectra demonstrate that the crystals grown by VS method have better quality that those grown using the VLS method, besides there is no remarkable difference in the quality of crystals grown by VLS method with the use of Au or Ag and on pure glass substrate *versus* glass covered with ITO film.

However, other data demonstrate that ITO may be not a neutral substrate. Fig. 4 exhibits the luminescent spectra for the samples grown by VLS method on ITO at different temperatures. The ratio of luminescent bands is 21.4 for the sample grown at 440 °C, while band-edge luminescence for the sample grown at 625 °C is practically invisible, and the ratio for this sample is 108.7.

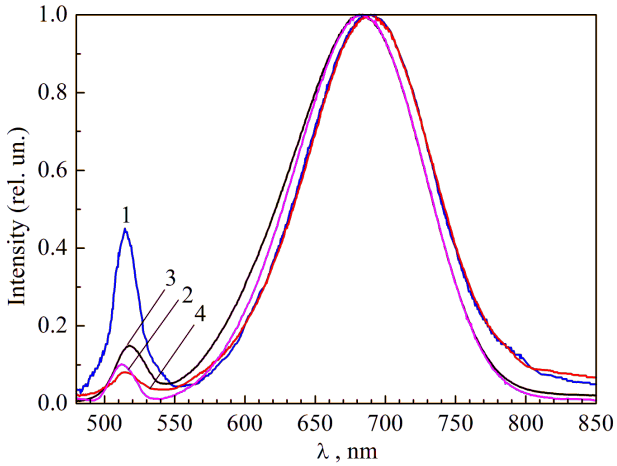


Fig. 3. Normalized luminescence spectra of CdS nanocrystals grown using the VS methods on glass (*1*) and VLS method with Au on glass (*2*), with Au on ITO (*3*) and with Ag on ITO (*4*).

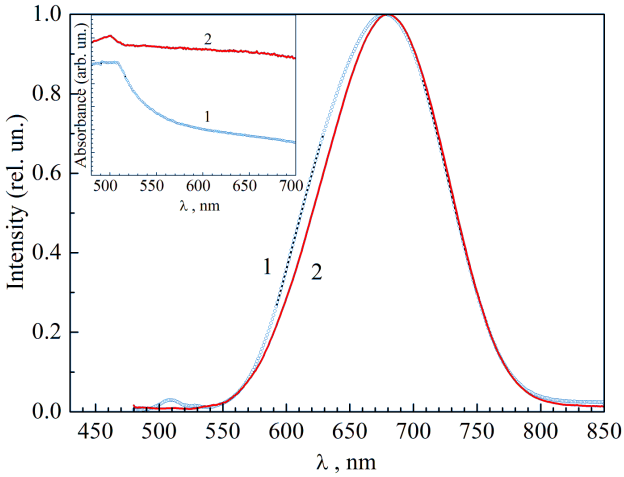


Fig. 4. Normalized luminescence spectra of the CdS samples grown by VLS method with Ag on ITO at 440 °C (*1*) and 625 °C (*2*). Insert demonstrates absorption of these samples.

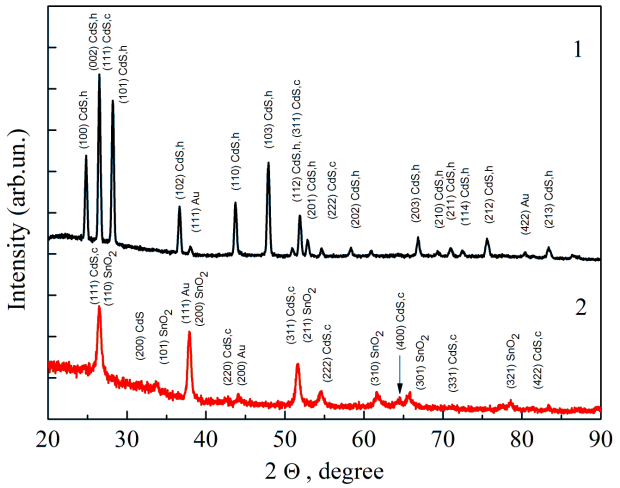
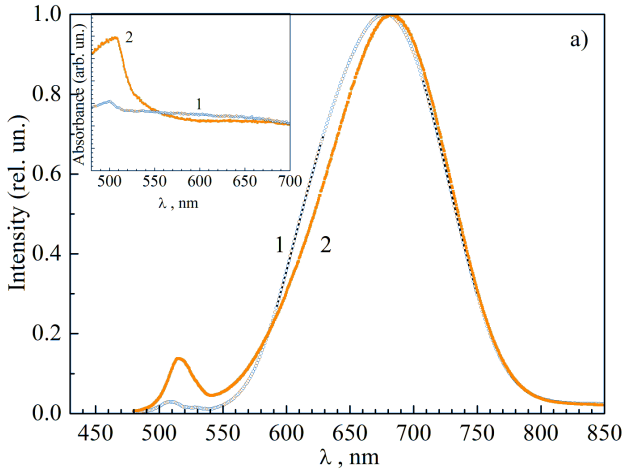


Fig. 5. X-ray diffraction measured on the CdS sample grown by the VS method (*1*) and on the CdS sample grown by the VLS method with Au on ITO (*2*) at the temperature 655 °C.



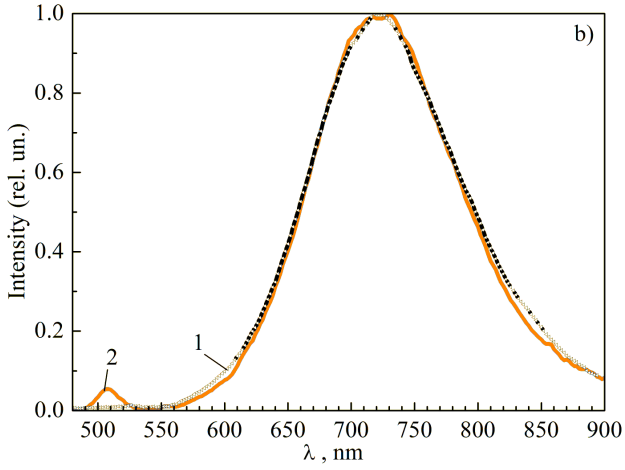


Fig. 6. Normalized luminescence spectra for the CdS samples grown using the VLS method (a) with Ag on ITO at 440 °C with the deficiency of sulfur (*1*) and at 475 °C with the sulfur compensation (*2*) and grown by the micro-crucible method on a pyrolytic carbon fiber without (*1*) and with (*2*) an additional source of sulfur (b). The insert in the panel (a) demonstrates absorption of these samples.

It means that ITO is not neutral at high temperature and is, probably, destructed resulting in the distortion of the crystal structure of grown CdS or increased impurity level. This is supported by the behavior of absorption of those samples shown in the insert. Again, we have to remind that there is no sense to discuss absolute values without knowledge of the amount of the material, but the spectral behavior of the absorption allows to make qualitative conclusion. The feature at about 510 nm corresponds to the absorption at the band edge what assumes crystal structure of the sample. So, we suppose that the steepness of that feature as well as the difference between the maximum and long-wave tail should correlate with perfectness of the crystal structure in this material. Thus, absorption also demonstrates that CdS grown on ITO at low temperature has a better crystal structure than CdS grown on ITO at high temperature. This conclusion is supported by XRD measurements, too, which results are shown in Fig. 5.

The results of X-ray diffraction demonstrate that the VS method results in CdS whiskers with a good crystal structure most probably of wurtzite type, which is marked with "h" index in Fig. 5. Only couple of lines is common for hexagonal and cubic "c" – sphalerite forms of CdS. It is also supported by Fig. 1a, which demonstrates whiskers grown using the VS method with a perfect crystal shape. The opposite situation is for the sample grown on ITO at high temperature. In this case, the spectrum demonstrates presence of preferentially SnO_2 and weak signal of sphalerite form of CdS.

Other sources of defect luminescence were analyzed, too. As it was indicated, an additional source of sulfur is necessary to keep stoichiometry of grown whiskers. Comparison of samples grown with the additional source of sulfur (S+) and without (S-) is demonstrated in Fig. 6.

It is visible that for different growth methods additional compensation of the sulfur deficiency improves

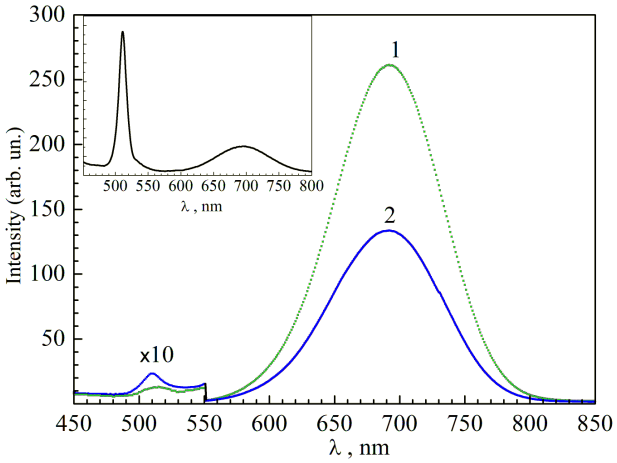


Fig. 7. Luminescence spectra of the CdS nanowhiskers grown by the VLS method with Au of different sizes of nuclei. The insert demonstrates the spectrum of CdS single crystal. The mass thickness of Au is 0.5 nm (*1*), 2.5 nm (*2*).

the quality of grown crystals. Ratios of the luminescent intensities in this case for the whiskers grown by the VLS method are 7.2 for the additional sulfur source (S+) and 21.4 without (S-), and in the case of micro-crucible growth those ratios are 18 (S+) and 111 (S-). It is difficult to say at the moment why micro-crucible growth produces crystals with so high defect luminescence in comparison to the band-edge one. For the case of VLS growth absorption, behavior correlates with the ratio of luminescence bands and supports again the conclusion about better quality of crystals grown with the additional sulfur source.

The latter analyzed case shows the influence of the surface area, which contribution rises with decreasing the diameter of grown nanowhiskers. Two samples grown by the VLS method with Au on glass are compared in Fig. 7.

The spectra shown in Fig. 7 were measured for the samples grown using the VLS method with Au deposited with different mass thickness. The sample with the mass thickness of Au 2.5 nm (*2*) and the average width of whiskers in hundreds of nanometers demonstrates obviously lower ratio of intensities of lines in comparison to the sample where the mass thickness of Au was 0.5 nm (*1*) and the average width of whiskers was tens of nanometers. These results coincide with previously published demonstration of increasing defect luminescence at decreasing of the sizes of nanocrystals [20]. For comparison, the spectrum of luminescence inherent to the single crystal is shown in the insert. In this case, band-edge luminescence exceeds the defect one.

It is necessary to note that all the demonstrated results cannot be considered as controversial and clearly demonstrating only some separated source as the origin of the defect luminescence. For example, the hypothesis that defect luminescent line is produced in the first place by sulfur vacancies concentrated at the surface and the speed of growth affects the concentration of those vacancies explains practically all the demonstrated results. Slower growth obviously allows repairing bigger number of defects of the crystal structure, so the VS method produces more quality crystals in comparison with the VLS method at other equal parameters.

4. Conclusions

We have demonstrated that luminescence can be used for the express control of the quality of CdS crystals grown by different technological approaches. The influence of different technological parameters has been analyzed from the viewpoint of their influence on the crystal quality. It has been shown that the defect luminescence correlates with the deficiency of sulfur and rises at the increasing of the surface. Also, slower growth using the VS method produces more qualitative crystals due to, obviously, more effective reparation of defects, what needs some time.

References

1. Zhang A., Zheng G., Lieber C., *Nanowires. Building Blocks for Nanoscience and Nanotechnology*. Springer, Switzerland, 2016. DOI: 10.1007/978-3-319-41981-7.
2. Li Y., Qian F., Xiang J., Lieber C.M. Nanowire electronic and optoelectronic devices. *Materials Today*. 2006. **9**, No 10. P. 18–27. https://doi.org/10.1016/S1369-7021(06)71650-9.
3. Dubrovskii V.G., Cirlin G.E., Ustinov V.M. Semiconductor nanowhiskers: Synthesis, properties, and applications. *Semiconductors*. 2009. **43**, No. 12. P. 1539–1584. https://doi.org/10.1134/S106378260912001X.
4. Pachauri V., Kern K., Balasubramanian K. Field-effect-based chemical sensing using nanowire-nanoparticle hybrids: The ion-sensitive metal-semiconductor field-effect transistor. *Appl. Phys. Lett*. 2013. **102**, No 2. 023501 (9 p). https://doi.org/10.1063/1.4775579.
5. Huang Y., Duan X., Lieber C.M. Nanowires for integrated multicolor nanophotonics. *Small.* 2005. **1**, No 1. P. 142–147. https://doi.org/10.1002/smll.200400030.
6. Couteau C., Larrue A., Wilhelm C., Soci C. Nanowire lasers. *Nanophotonics*. 2015. **4**. P. 90–107. https://doi.org/10.1515/nanoph-2015-0005.
7. Li L., Lou Z., Shen G. Hierarchical CdS nanowires based rigid and flexible photodetectors with ultrahigh sensitivity. *ACS Appl. Mater. Interfaces*. 2015. **7**, No.42. P. 23507–23514. https://doi.org/10.1021/acsami.5b06070.
8. Zhu L., Feng C., Li F. et al. Excellent gas sensing and optical properties of single-crystalline cadmium sulfide nanowires. *RSC Adv*. 2014. **4**, No 106. P. 61691–61697. https://doi.org/10.1039/C4RA11010B.
9. Ramgir N.S., Yang Y., Zacharias M. Nanowire-based sensors. *Small*. 2010. **6**, No 16. P. 1705–1722. https://doi.org/10.1002/smll.201000972.

10. Patolsky F., Lieber C.M. Nanowire nanosensors. *Materials Today*. 2005. **8**, No 4. P. 20–28. https://doi.org/10.1016/S1369-7021(05)00791-1.
11. Garnett E.C., Brongersma M.L., Cui Y., McGehee M.D. Nanowire solar cells. *Annu. Rev. Mater. Res.* 2011. **41**. P. 269–295. https://doi.org/10.1146/annurev-matsci-062910-100434.
12. Agata M., Kurase H., Hayashi S., Yamamoto K. Photoluminescence spectra of gas-evaporated CdS microcrystals. *Solid State Commun*. 1990. **76**, No 8. P. 1061–1065. https://doi.org/10.1016/0038-1098(90)90084-O.
13. Artemyev M.V., Sperling V., Woggon U. Electroluminescence in thin solid films of closely packed CdS nanocrystals. *J. Appl. Phys*. 1997. **81**, No 10. P. 6975–6977. https://doi.org/10.1063/1.365261.
14. Li H., Wang X., Xu J., Zhang Q., Bando Y., Golberg D., Ma Y., Zhai T. One-dimensional CdS nanostructures: A promising candidate for optoelectronics. *Adv. Mater*. 2013. **25**. P. 3017–3037. https://doi.org/10.1002/adma.201300244.
15. Georgobiani A.N., Sheynkman M.K. (eds.) *The Physics of $A^{II}B^{VI}$ Compounds*. Moscow, Nauka, 1986 (in Russian).
16. Grynko D.A., Fedoryak A.N., Dimitriev O.P., Lin A., Laghumavarapu R.B., Huffaker D.L. Growth of CdS nanowire crystals: Vapor–liquid–solid versus vapor–solid mechanisms. *Surface and Coatings Technology*. 2013. **230**. P. 234–238. https://doi.org/10.1016/j.surfcoat.2013.06.058.
17. Sears G.W. A mechanism of whisker growth. *Acta Metal*. 1955. **3**. P. 367–369. https://doi.org/10.1016/0001-6160(55)90042-0.
18. Grynko D.O., Fedoryak A.N., Smertenko P.S., Dimitriev O.P., Ogurtsov N.A., Pud A.A. Hybrid solar cell on a carbon fiber. *Nanoscale Res. Lett*. 2016. **11**, No 1. P. 265–274. https://doi.org/10.1186/s11671-016-1469-7.
19. Liu W., Jia C., Jin C., Yao L., Cai W., Li X. Growth mechanism and photoluminescence of CdS nanobelts on Si substrate. *J. Cryst. Growth*. 2004. **269**, No 2-4. P. 304–309. https://doi.org/10.1016/j.jcrysgro.2004.05.093.
20. Mochizuki K., Satoh M., Igaki K. Orange luminescence in CdS. *Jpn. J. Appl. Phys*. 1983. **22**, No. 9. P. 1414–1417. https://doi.org/10.1143/JJAP.22.1414.
21. Veamatahau A., Jiang B., Seifert T. et al. Origin of surface trap states in CdS quantum dots: Relationship between size dependent photoluminescence and sulfur vacancy trap states. *Phys. Chem. Chem. Phys*. 2015. **17**. P. 2850–2858. https://doi.org/10.1039/C4CP04761C.
22. Liang S., Li M., Wang J.-H., Liu X.-L., Hao Z.-H., Zhou L., Yu X.-F., Wang Q.-Q. Silica-coated and annealed CdS nanowires with enhanced photoluminescence. *Opt. Exp*. 2013. **21**, No 3. P. 3253–3258. https://doi.org/10.1364/OE.21.003253.
23. Liu B., Chen R., Xu X.L. et al. Exciton-related photoluminescence and lasing in CdS nanobelts. *J. Phys. Chem. C*. 2011. **115**. P. 12826–12830. https://doi.org/10.1021/jp203551f.

Authors and CV

Alla Bogoslovskaya, Senior scientific researcher at the Department of Physics of Optoelectronic devices, V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine. The area of scientific interests includes physics and technology of semiconductor nanostructured materials and device structures of optoelectronics.

Oleksandr Gudymenko, Senior researcher at the Department of Structural and Elemental Analysis of Materials and Systems at the V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. His research interests include: solid-state physics, dynamical theory of diffraction of radiation, X-ray optics, X-ray diffraction analysis of semiconductor crystals, hetero- and nanosystems.

Eugene Bortchagovsky had graduated the Moscow Institute of Physics and Technologies and since 1983 he has been working at the Institute of Semiconductor Physics of NAS of Ukraine. He obtained PhD in 1991 and DrSc in Physics in 2016. At the moment E.G. Bortchagovsky is the head of the laboratory of the optoelectronic molecular-semiconducting systems.

Dmytro Grynko, Senior researcher at the Department of Functional Materials and Nanostructures (*laboratory of the optoelectronic molecular-semiconducting systems*) at the V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine. Scope of current research interests: functional molecular, low-dimensional nanostructures and nanocomposite nanostructured thin film media, gas-phase technology and application, template guided self-organization, technology of low-dimensional structures, nanosize single crystals. Technical experience*:* nanowires, nanosize single crystals growth from gas-phase; gas-phase technology for multicomponent nanocomposites films based on fullerenes, organic dyes, organic polymer and non-organic compounds; CVD, organometallic compounds.