

Reply to Kavetsky and Stepanov's "Comments on the "Metallic nanoparticles (Cu, Ag, Au) in chalcogenide and oxide glassy matrices: comparative assessment in terms of chemical bonding"

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Authors notes

In their "Comments ..." [1], the authors T.S. Kavetsky and A.L. Stepanov [1] claim on "... ion-synthesized Cu nanoparticles in chalcogenide glasses" as perfect and entirely proved fact, but surprisingly doubt on sizes of these nanoparticles. They reject relation to their previous conclusion on similarities in surface plasmon resonance as resulting from similar agglomeration of nanoparticles in ion-implanted oxide and chalcogenide matrices [2-4], explaining this misunderstanding as originated from "restricted information" in their previous references. They also reject direct pointing on sizes of agglomerated nanoparticles (5...10 nm in radius) reported by Kavetsky in conference materials [5], nominating this statement only as assumption (*i.e.*, meaningless – auth.). However, as a matter of fact, all these speculations on expected particle sizes (5...10 nm in radius as really assumed in [5] and later recited by us in [6], or other more indefinite ones [2-4]) have no any relation to the problem on appearance of metallic (Cu) nanoparticles as a result of destructive embedding in chalcogenide glass matrices under low-energy ion implantation. In their previous papers [2-4], the authors of "Comments ..." stated on principal possibility to form such "... ion-synthesized Cu nanoparticles in chalcogenide glasses" like it occurs in oxides, such as vitreous silica SiO₂, in part [6]. Moreover, in [4], these authors announced that "... the formation of Cu nanoparticles" in As₂S₃ and Ge_{15.8}As₂₁S_{63.2} glasses was confirmed due to EDX analysis.

In an obvious contrast to these allegations, we have proved impossibility to do this in "soft" covalent networks of chalcogenide glasses under *destructive*

embedding of metallic additives [7]. The numerical χ -*criterion* describing disproportionality in chemical bonding of metal-activated matrices is shown to be more than one-order smaller in typical chalcogenide environment (As-S/Se or Ge-S/Se) than in oxide (Si-O) one. This means impossibility of destructed chalcogenide networks to accommodate agglomerates of "pure" metallic nanoparticles without forming competitive metal-chalcogenide compounds. But, this is not a case of "hard" oxide glasses with evidently stronger *host* chemical bonding as compared with *guest* metal oxides [8-10]. In this respect, it will be not surprising, if "... ion-synthesized Cu nanoparticles in chalcogenide glasses" as announced by Kavetsky *et al.* [2] occur to be realistically only "the Cu chalcogenide particles". Therefore, it seems reasonable to ask, where do the authors [1] really stand on this controversy? Do they understand principal difference between "... ion-synthesized Cu nanoparticles" (*viz.*, the "pure" Cu particles agglomerated in the glass) and "Cu-ion-implanted As₂S₃ glass" (*viz.*, the glass of As₂S₃ composition disturbed anyhow by implanted ions)?

It is quite understandable that disproportionality of chemical bonds determined by interaction between unfettered atoms of *host* glass and embedded *guest* metallic atoms in respect to χ -*criterion* [7] is defined merely by destruction of glassy matrix, but not depth of ion implantation (or average energy of implanted ions penetrating into glass up to tens nm), as inconsistently declared in "Comments ..." [1]. Even under small penetration depth of implanted ions (near ~60 nm), attempts to ascribe under-margin (if any) changes in optical transmission and Z-scan curves of As₂S₃ glass to

effect of polishing procedure having "... uncontrolled impact on the homogeneous structure of glass in the near-surface region" seems absolutely misleading. Indeed, any polishing procedure fails to explain ~70 nm short-wave shift in optical transmission edge for 1-mm As₂S₃ glass in [2, 4] (as compared with the known data [11, 12], this "effect" questioning that tested glass in [2, 4] was really stoichiometric As₂S₃), as well as point-by-point coincidence (excepting 580...590 nm) in optical transmission for initial and implanted glasses [2]. Finally, and most consistently, there is no any reason to believe in enhanced optical non-linearity in ion-implanted glass in [2], since Z-scan patterning was not performed for initial (non-implanted) sample.

References

1. Kavetsky T.S., Stepanov A.L. Comments on the "Metallic nanoparticles (Cu, Ag, Au) in chalcogenide and oxide glassy matrices: comparative assessment in terms of chemical bonding". *Semiconductor Physics, Quantum Electronics & Optoelectronics*. 2017. **20**, No 1. P. 26–33.
2. Kavetsky T.S., Valeev V.F., Nuzhdin V.I., Tsmots V.M., Stepanov A.L. Optical properties of chalcogenide glasses with ion-synthesized copper nanoparticles. *Techn. Phys. Lett.* 2013. **39**, No 1. P. 1–4.
3. Kavetsky T., Stepanov A.L., Bazarov V.V., Tsmots V., Ren J., Chen G., Zhao X. Comparative study of optical properties of polarizing oxide glasses with silver nanorods and chalcogenide glasses with copper nanoparticles. *Phys. Procedia*. 2013. **48**. P. 191–195.
4. Kavetsky T.S., Stepanov A.L. Effects of gamma-irradiation and ion implantation in chalcogenide glasses. Chapter 14. In: *Glass Nanocomposites: Synthesis, Properties and Applications* (B. Karmakar, K. Rademann, A.L. Stepanov, eds.). Elsevier Academic Press, 2016. P. 341–358.
5. Kavetsky T.S., Tsmots V.M., Stepanov A.L. Optical properties of chalcogenide and oxide glasses with ion-synthesized metal nanoparticles. VI *Ukrainian scientific conference on physics of semiconductors*. Abstracts of reports. Chernivtsi, Ukraine, September 30 – October 4, 2013, P. 500 (in Ukrainian).
6. Stepanov A.L., Galyautdinov M.F., Evlyukhin E.A., Nuzhdin V.I., Valeev V.F., Osin Y.N., Evlyukhin A.B., Kiyani R., Kavetsky T.S., Chichkov B.N. Synthesis of periodic plasmonic microstructures with copper nanoparticles in silica glass by low-energy ion implantation. *Appl. Phys. A: Mater. Sci. Process.* 2013. **111**. P. 261–264.
7. Shpotyuk O.I., Vakiv M.M., Shpotyuk M.V., Kozyukhin S.A. Metallic nanoparticles (Cu, Ag, Au) in chalcogenide and oxide glassy matrices: comparative assessment in terms of chemical bonding. *Semiconductor Physics, Quantum Electronics & Optoelectronics*. 2017. **20**, No 1. P. 26–33.
8. Borisova Z. U., Bychkov U.F., Tver'yanovich Yu.S. Interaction of metals with chalcogenide glasses. Leningrad, Publ. in Leningrad University, 1991.
9. Tanaka K., Shimakawa K. Amorphous chalcogenide semiconductors and related materials. New York–Dordrecht–Heidelberg–London: Springer.
10. Musgraves J.D., Richardson K., Jain H. Laser-induced structural modification, its mechanisms, and applications in glassy optical materials. *Opt. Mater. Exp.* 2011. **1**. P. 921–935.
11. Shpotyuk M., Shpotyuk O., Golovchak R., McCloy J., Riley B. Compositional trends of γ -induced optical changes observed in chalcogenide glasses of binary As-S system. *J. Non-Cryst. Sol.* 2014. **386**. P. 95–99.
12. Shpotyuk O.I. Chapter 6. Radiation-induced effects in chalcogenide vitreous semiconductors. In: *Semiconducting Chalcogenide Glass I: Glass Formation, Structure, and Stimulated Transformations in Chalcogenide Glasses: Semiconductors and Semimetals*, Vol. 78 (R. Fairman and B. Ushkov, eds.). Elsevier Acad. Press, Amsterdam–Boston–London–New York–Oxford–Paris–San Diego–San Francisco–Singapore–Sydney–Tokyo, 2004. P. 215–260.