Electronics and Information Technologies, 2025, 31, 137–144
http://publications.lnu.edu.ua/collections/index.php/electronics/index

UDC: 538.9

ELECTRONIC PROPERTIES OF Ga-DOPED As-Se-Te GLASSES

Yaroslav Shpotyuk*[1]*, Adam Ingram*[2]*, Andriy Luchechko*[1]*,
Dmytro Slobodzyan*[1]*, Markiyan Kushlyk*[1]*, Oleh Kravets*[1]*,
***Mykhaylo Shpotyuk*[1]*, Roman Golovchak*[3]**
[1]Department of Sensor and Semiconductor Electronics,
Ivan Franko National University of Lviv,
107, Tarnavskoho Str., 79017 Lviv, Ukraine
[2]Department of Physics, Opole University of Technology,
75, Ozimska str., Opole, 45370, Poland
[3]Department of Physics, Engineering and Astronomy, Austin Peay State University,
Clarksville, TN 37044, USA
**Corresponding author e-mail: yaroslav.shpotyuk@lnu.edu.ua*

Shpotyuk, Y., Ingram, A., Luchechko, A., et al. (2025). Electronic Properties of Ga-doped As-Se-Te Glasses. *Electronics and Information Technologies*, 31, 137–144. https://doi.org/10.30970/eli.31.12

ABSTRACT

Introduction. The As-Se-Te system attracts significant attention since these chalcogenide glasses are endowed with unique semiconductor and optical characteristics. The wide infrared transparency, non-linearity, and ease of molding capability in these glasses render them promising candidates for electronic and photonic applications. However, the solubility of rare earth ions in chalcogenide matrices is generally low, restricting their applications. The addition of Ga is known to improve apparent solubility, but the intrinsic electrical characteristics of Ga-doped As-Se-Te glasses remain unexplored.

Materials and Methods. Chalcogenide glasses of the As-Se-Te system doped with Ga were explored. Samples were obtained from high-purity precursor using the melt-quenching method. Optical, structural, and electronic properties of the studied samples were investigated using high-resolution X-ray photoelectron spectroscopy (XPS), impedance spectroscopy, and optical spectroscopy.

Results. The incorporation of both Ga and Te leads to a decrease in the optical bandgap compared to binary As_2Se_3 glass. The valence band XPS spectra of the studied glasses reveal characteristic features similar to other binary and ternary chalcogenides, reflecting contributions from Se, Te, As, and Ga electronic states. These results indicate that the electronic structure is strongly influenced by chalcogen–As(Ga) bonding, which affects the valence band density of states and associated defect-related phenomena. The temperature-dependent DC conductivity demonstrates multiple conduction mechanisms. Incorporation of Ga lowers the high-temperature activation energy slightly, indicating modifications of the conduction process, while Te-containing samples exhibit even higher activation energies, suggesting contributions from hopping mechanisms and defect-related states.

Conclusions. The influence of Ga and Te on the optical and electronic properties of As_2Se_3-based chalcogenide glasses is studied using optical and impedance spectroscopies. Electronic properties of Ga-modified As-Se-Te glasses are shown to be important for their applications in optoelectronic integrated platforms. The obtained results are correlated to the valence band structure of these materials determined through XPS.

Keywords: chalcogenide glass, DC conductivity, bandgap, temperature dependence.

INTRODUCTION

Arsenic-selenium-tellurium glasses are important functional materials for active and passive applications in modern photonic and electronic integrated platforms thanks to their high infrared (IR) transparency, excellent fiber drawing and molding capabilities, simple thin-film technology, large optical nonlinearities, and presence of semiconductor properties. The common examples include far-IR optics, IR optical waveguides for space telecommunication, chemical and biological sensors, phase-change devices, and Ovonic switches [1-8]. More applications are possible if these glasses are doped with rare-earth elements, such as Ce, Pr, Eu, Tb, Dy, or Er, enabling active media for lasers, optical amplifiers, and broadband sources in the mid-IR spectral range [3,9,10]. The bottleneck of such applications is a concentration of rare-earth ions, whose solubility in chalcogenide matrices is generally low, because at higher concentrations, the rare-earth atoms clamp into metal nanoparticles. Ga is known to improve the number of rare-earth atoms converted into the ionic form, increasing their apparent solubility [11,12].

Recently, the influence of Ga on the structure of arsenic selenides and arsenic-tellurium selenides has been investigated [13,14], whereas the basic electrical properties of these glasses remain unexplored. So, in the present work, we have performed optical and electrical characterization of As-Se-Te glasses containing 2 at.% of Ga, and binary As-Se glasses with a variable concentration of Ga.

MATERIALS AND METHODS

A conventional melt-quench method was employed for the synthesis of $Ga_x(As_{0.4}Se_{0.6})_{100-x}$ (x=0,1,2,3,4,5) and $Ga_2(As_{0.4}Se_{0.6})_{98-y}Te_y$ (y=0,10,15,20,30) glasses using high-purity (at least 5N) chemical precursors: Ga, As, Se, and Te. Melting was performed in a vacuum-sealed silica tube at 900 °C for 10 hours using a rocking furnace. After quenching into water from 750 °C, the samples were annealed for 6 h, at ~10 °C below the corresponding glass transition temperatures.

High resolution XPS valence band spectra were recorded with a Scienta ESCA-300 spectrometer (monochromatic Al K_α X-rays) on the samples fractured *in situ* in the spectrometer's measurement chamber under a vacuum of 2×10^{-8} Torr or better. For all measurements, the angle between the surface and detector was 90°. The instrument was operated in a mode that yielded a Fermi-level width of 0.4 eV for Ag metal and at a full width at half maximum of 0.54 eV for the Ag $3d_{5/2}$ core level peak. The energy scale was calibrated using the Fermi level of clean Ag. Surface charging from the photoelectron emission was neutralized using a low-energy (<10 eV) electron flood gun. The experimental positions of the valence band spectra were adjusted by referencing to the position of the 1*s* core level peak (284.6 eV) of adventitious carbon [15]. XPS data were analyzed with the standard CASA-XPS software package.

Temperature-dependent Direct Current (DC) conductivity measurements were performed in vacuum using an HIOKI LCR impedance analyzer with a bias voltage of 1 V. Carbon paste electrodes were deposited on the opposite sides of 1 mm thick sample disks to create an electrical ohmic contact.

Optical transmission spectra were recorded at room temperature by Agilent Technologies Cary-5000 UV/Vis/NIR spectrometer in the 200–3200 nm spectral range with 2 nm resolution.

RESULTS AND DISCUSSION

The fundamental optical absorption edges of the investigated $Ga_x(As_{0.4}Se_{0.6})_{100-x}$ and $Ga_2(As_{0.4}Se_{0.6})_{98-y}Te_y$ glasses are shown in **Fig. 1**, where the absorption coefficient (α) was calculated from the transmission data of bulk 2 mm thick samples with the aid of PARAV software [16].

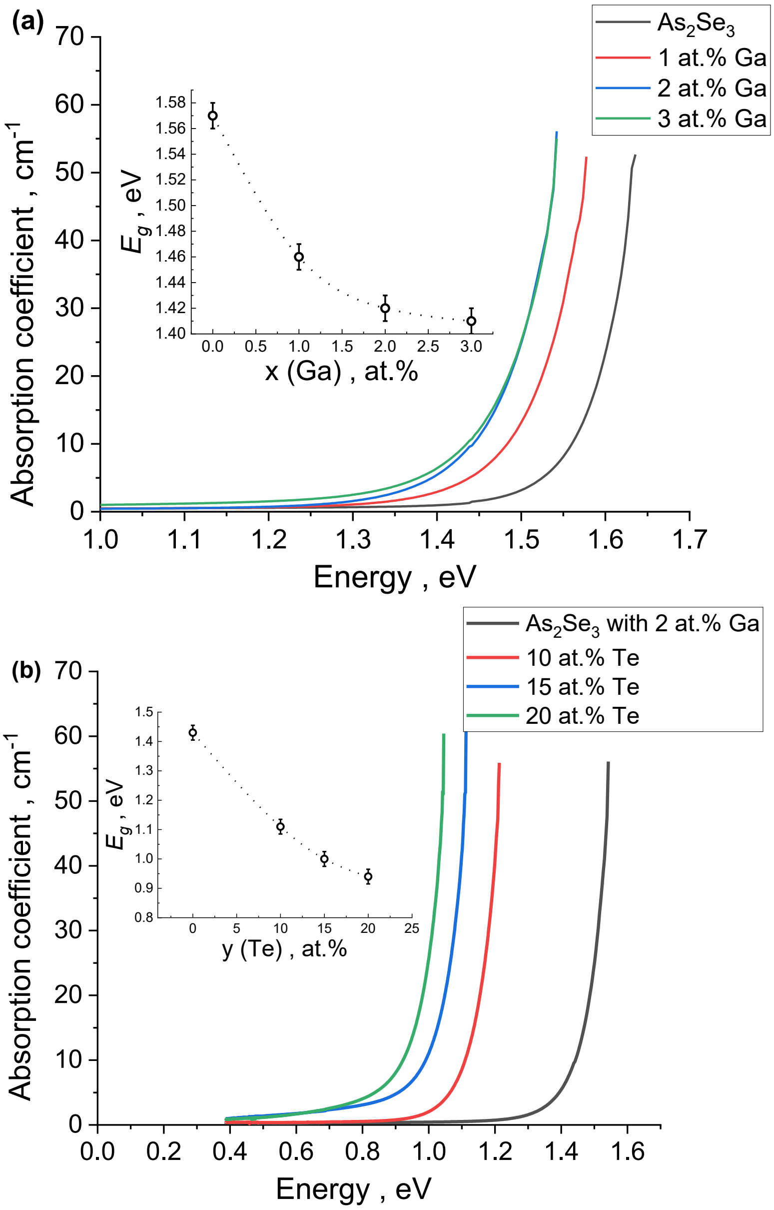

Fig. 1. Optical absorption coefficients of Ga$_x$(As$_{0.4}$Se$_{0.6}$)$_{100\text{-}x}$ (a) and Ga$_2$(As$_{0.4}$Se$_{0.6}$)$_{98\text{-}y}$Te$_y$ (b) bulk glasses calculated from room-temperature transmission spectra. The inserts show estimated optical bandgap compositional dependences.

The edge follows the expected Urbach exponential behaviour proper to most chalcogenide glasses [17,18]. The inserts show optical bandgap (E_g) values and their compositional dependence, estimated using Tauc plots for the indirect electron transitions in PARAV [16].

$$\alpha h\nu = B(h\nu - E_g)^2 \qquad (1)$$

The room-temperature optical bandgap values drop from ~1.6 (±0.05) eV for As$_2$Se$_3$ glass to ~1.4 (±0.1) eV for Ga-modified As$_2$Se$_3$, and to ~1.0 (±0.1) eV with Te addition. So, incorporation of both Ga and Te leads to a decrease in the optical bandgap compared to binary As_2Se_3 glass, the effect of Te being more significant.

The classic DC conductivity (σ_{DC}) *vs* $1/T$ dependence of chalcogenide glasses shows several distinct regions [17-19]. The high-temperature one is associated with charge carriers excited directly into the non-localized states of the conduction band (E_c). It is followed by the region where charge carriers are excited into localized states (E_A) near the edge of the conduction band or localized states (E_B) near the edge of the valence band (E_v). They usually contribute to a hopping mechanism of charge transport. There could also be a region associated with temperature-activated hopping of charge carriers localized in the states at the Fermi level (E_F), if present. All these mechanisms follow $\exp(-E_a/kT)$ dependence, where activation energy E_a depends on E_A, E_B, E_c, E_v, E_F and activation energies of charge hopping (W_i) between relevant localized states [18]. Finally, the low-temperature region usually follows the well-known $T^{-1/4}$ law and is ascribed to a temperature-activated hopping of charge carriers with variable jump lengths (variable range hopping) [18].

The slopes of the linear fits to the high-temperature region of $\ln(\sigma_{DC})$ *vs* $1/T$ dependences (**Fig. 2**) were used to determine the relevant activation energies. Calculated high-temperature value of $E_a = 0.85\ (\pm 0.05)$ eV for As_2Se_3 bulk sample roughly corresponds to a half of the optical bandgap (or slightly higher), which allows us to assume (if one accepts that Fermi level in chalcogenide glasses is pinned near the middle of bandgap) [17,18] that this conduction mechanism is associated with direct excitation of charge carriers into the non-localized states of conduction band with $E_a = E_c - E_F$. Incorporation of Ga into As_2Se_3 bulk glass decreases the value of $E_a = 0.75\ (\pm 0.02)$ eV while still being close to half of the corresponding optical bandgap of Ga-modified As_2Se_3 samples. Nevertheless, these values are consistently higher than one half of the corresponding optical bandgap values, which might indicate a slight shift of the Fermi level towards the valence band in full agreement with the fact that most chalcogenides are generally considered as *p*-type semiconductors [17,20]. This difference is even more pronounced in Te-containing samples, where doubled E_a values (E_a decreases from 0.67 to 0.60 eV with Te addition) are noticeably higher than E_g values (1.0±0.1 eV, see insert to **Fig. 1b**). The higher activation energies than the half of the optical bandgap values can also originate from the hopping mechanism of conduction involving localized states with $E_a = E_{A,B} - E_F + W_i$, where W_i is the hopping activation energy [18]. The latter mechanism can also be a reason for a kink in conductivity dependences like the one visible after $1000/T \sim 3$ for some of the investigated glass compositions, including As_2Se_3 (**Fig. 2**). The hopping mechanism relies on a higher concentration of defects, like D^+-D^- topological

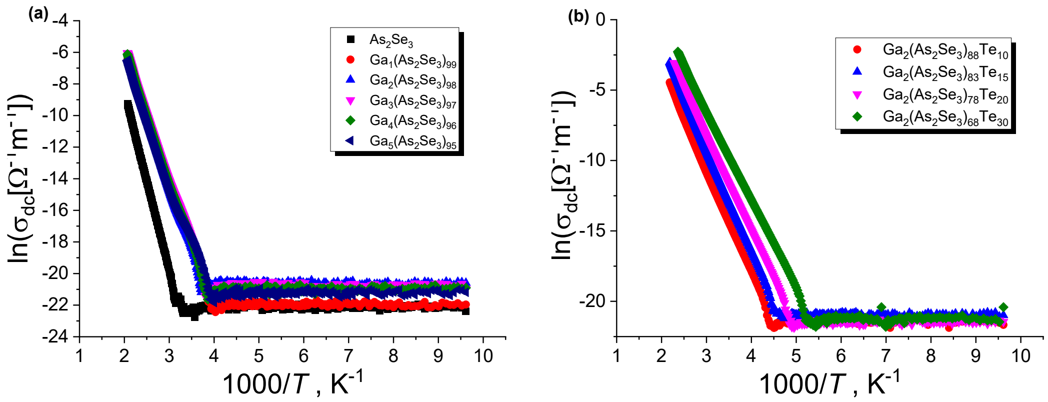

Fig. 2. Temperature dependence of DC conductivity for $Ga_x(As_{0.4}Se_{0.6})_{100-x}$ (a) and $Ga_2(As_{0.4}Se_{0.6})_{98-y}Te_y$ (b).

coordination centres, used to explain many phenomena in vitreous chalcogenides [17,18]. At the same time, the low-temperature region of $T^{-1/4}$ dependence is difficult to assess in the samples investigated due to very low conductivity values, which are on the verge of equipment sensitivity.

The valence band density of states is crucial for the understanding of electronic properties, defect structure, and various induced phenomena occurring in chalcogenide glasses [17-21]. Valence band XPS spectra of the investigated samples (**Fig. 3**) show similar features to the valence bands of other binary and ternary chalcogenides [22]. The well-observed feature at about 2 eV is attributed to the lone pair Se 4*p* and Te 5*p* (in Te-containing samples) electrons, whereas the peak at about 5 eV is contributed by 4*p* and 5*p* bonding states of Se and Te (if present in the composition), respectively. The observed broad band at 7-16 eV is due to the overlap of signals from Ga 4*s*, As 4*s*, Se 4*s* and Te 5*s* electrons, whereas XPS signal at 18 eV is caused by Ga 3*d* electrons (**Fig. 3**). The valley at ~3 eV, which is well observed in Se-rich arsenic selenides [22], disappears in the investigated glasses due to the broadening of Se 4*p* and Te 5*p* XPS peaks by As 4*p* and Ga 4*p* bonding states from a prevailing concentration of chalcogen-As(Ga) bonds.

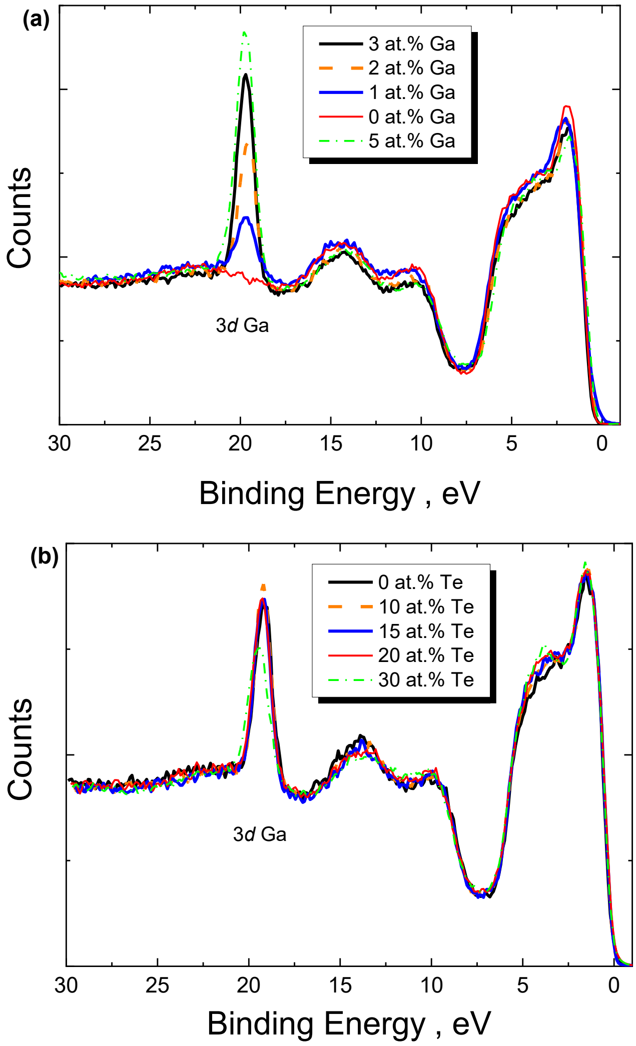

Fig. 3. Valence band XPS spectra recorded for a fractured in vacuum $Ga_x(As_{0.4}Se_{0.6})_{100-x}$ (a) and $Ga_2(As_{0.4}Se_{0.6})_{98-y}Te_y$ (b) bulk glasses.

CONCLUSION

Incorporation of Ga into As_2Se_3 glass matrix leads to a decrease in its optical bandgap and activation energy of high-temperature DC conductivity. Further addition of Te into the composition leads to a more significant decrease in the optical bandgap and activation energy of DC electrical conductivity. Valence band XPS spectra correlate well with the electrical and optical properties of the investigated materials, showing typical features of chalcogenide vitreous semiconductors.

ACKNOWLEDGMENTS AND FUNDING SOURCES

This work was performed within the framework of the IMPRESS-U project supported by the NSF (Grant # OISE-2106457), NAWA (Grant # BPN/NSF/2023/1/00002/U/00001), and NAS (STCU Grant # 7112). This work is part of the research performed within projects No. 0123U100655 and 0125U000544, the subject of the Program funded by the Ministry of Education and Science of Ukraine.

COMPLIANCE WITH ETHICAL STANDARDS

The authors declare that the research was conducted in the absence of any potential conflict of interest.

AUTHOR CONTRIBUTIONS

Conceptualization, [Y.S., A.I., D.S., R.G.]; methodology, [Y.S., A.L., M.S., R.G.]; validation, [Y.S., A.I., R.G.]; formal analysis, [D.S., M.K.]; investigation, [Y.S., A.I., O.K., R.G.]; resources, [Y.S., M.S., R.G.]; data curation, [Y.S., A.I., D.S., R.G.]; writing – original draft preparation, [Y.S., R.G.]; writing – review and editing, [A.L., M.K., M.S.]; visualization, [Y.S., O.K., R.G.]; supervision, [Y.S., R.G.]; project administration, [Y.S., R.G.].

REFERENCES

[1] Seddon, A.B., Farries, M.C., Nunes J.J., Xiao, B., Furniss D., Barney, E., Phang, S., Chahal, S., Kalfagiannis, N., Sojka, Ł. & Sujecki, S. (2024). Short review and prospective: chalcogenide glass mid-infrared fibre lasers. *Eur. Phys. J. Plus, 139,* 142. https://doi.org/10.1140/epjp/s13360-023-04841-1

[2] Musgraves, J.D. (2024) Chalcogenide glasses: Engineering in the infrared spectrum. *American Ceramic Society Bulletin*, *103*(4), 22. https://bulletin.ceramics.org/article/chalcogenide-glasses-engineering-in-the-infrared-spectrum/

[3] Adam, J-L. & Zhang X. (2014). Chalcogenide Glasses: Preparation, properties and application*. Oxford, Cambridge: Woodhead Publishing series in Electronic and Optical Materials*, 704. ISBN 0857093568, 9780857093561

[4] Golovchak, R., Plummer, J., Kovalskiy, A., Holovchak, Y., Ignatova, T., Trofe, A., Mahlovanyi, B., Cebulski, J., Krzeminski, P., Shpotyuk, Y., Boussard-Pledel, C. & Bureau, B. (2023). Phase-change materials based on amorphous equichalcogenides. *Scientific Reports, 13*, 2881. https://doi.org/10.1038/s41598-023-30160-7

[5] Fritzsche, H. (2007). Why are chalcogenide glasses the materials of choice for Ovonic switching devices? *Journal of Physics and Chemistry of Solids, 68*, 878–882. https://doi.org/10.1016/j.jpcs.2007.01.017

[6] Cui, S., Chahala, R., Shpotyuk, Y., Boussard, C., Lucas, J., Charpentier, F., Tariel, H., Loréal, O., Nazabal, V., Sire, O., Monbet, V., Yang, Z., Lucas, P. & Bureau, B. (2014). Selenide and telluride glasses for mid-infrared bio-sensing. *Proceedings of SPIE, 8938*, 893805. https://doi.org/10.1117/12.2036734

[7] Eggleton, B.J., Luther-Davies, B. & Richardson, K. (2011). Chalcogenide photonics. *Nature Photonics, 5*, 141–148. https://doi.org/10.1038/nphoton.2011.309

[8] Yu, Q., Wang, Sh., Fu, Y., Tan, L., Gao, Ch., Lin, Ch. & Kang, Sh. (2024). Highly Er^{3+}-doped chalcogenide glass with enhanced mid-infrared emission and superior mechanical property. *Optics Express, 32*(26), 46131-46139. https://doi.org/10.1364/OE.544914

[9] Blanc, W., Choi, Y.G., Zhang, X., Nalin, M., Richardson, K.A., Righini, G.C., Ferrari, M., Jha, A., Massera, J., Jiang, S., Ballato, J. & Petit, L. (2023). The past, present and future of photonic glasses: A review in homage to the United Nations International Year of Glass 2022. *Progress in Materials Science, 134*, 101084. https://doi.org/10.1016/j.pmatsci.2023.101084

[10] Seznec, V., Ma, H., Zhang, X., Nazabal, V., Adam, J.-L., Qiao, X.S. & Fan, X.P. (2006). Spectroscopic properties of Er^{3+}-doped chalcohalide glass ceramics. *Proceedings of SPIE, 6116*, 61160B–1–9. https://doi.org/10.1117/12.645909

[11] Aitken, B.G., Ponader, C.W., & Quimby, R.S. (2002). Clustering of rare earths in Ge–As sulfide glass. *Comptes Rendus Chimie, 5(12)*, 865-872. https://doi.org/10.1016/S1631-0748(02)01458-3

[12] Choi, Y.G., Kim, K.H., Lee, B.J., Shin, Y.B., Kim, Y.S. & Heo, J. (2000). Emission properties of the Er^{3+}:$^4I_{11/2}\rightarrow{}^4I_{13/2}$ transition in Er^{3+}- and Er^{3+}/Tm^{3+}-doped Ge–Ga–As–S glasses. *Journal of Non-Crystalline Solids, 278,* 137-144. https://doi.org/10.1016/S0022-3093(00)00331-8

[13] Shpotyuk, Y., Bureau, B., Boussard-Pledel, C., Nazabal, V., Golovchak, R., Demchenko, P. & Polovynko, I. (2014). Effect of Ga incorporation in the $As_{30}Se_{50}Te_{20}$ glass. *Journal of Non-Crystalline Solids, 398–399*, 19–25. https://doi.org/10.1016/j.jnoncrysol.2014.04.021

[14] Shpotyuk, Y., Boussard-Pledel, C., Nazabal, V., Chahal, R., Ari, J., Pavlyk, B., Cebulski, J., Doualan, J.L. & Bureau, B. (2015). Ga-modified As_2Se_3–Te glasses for active applications in IR photonics. *Optical Materials, 46*, 228–232. https://doi.org/10.1016/j.optmat.2015.04.024

[15] Moulder, J.F., Stickle, W.F., Sobol, P.E. & Bomben, K.D. (1992). *Handbook of X-ray photoelectron spectroscopy* (J. Chastein, Ed.). Eden Prairie, MN: Perkin-Elmer Corp., Physical Electronics Division. Retrieved from https://www.phi.com/

[16] Ganjoo, A. & Golovchak, R. (2008). Computer program PARAV for calculating optical constants of thin films and bulk materials: Case study of amorphous semiconductors. *Journal of Optoelectronics and Advanced Materials, 10*, 1328–1332. Retrieved from http://joam.inoe.ro/

[17] Feltz, A. (1993). *Amorphous inorganic materials and glasses*. Weinheim, Germany: VCH, 477. ISBN 3527284214, 9783527284214.

[18] Mott, N.F. & Davis, E.A. (1979). *Electronic processes in non-crystalline materials*. Oxford, England: Clarendon Press.

[19] Golovchak, R., Plummer, J., Kovalskiy, A., Ingram, A., Kozdras, A., Ignatova, T., Trofe, A., Boussard-Pledel, C. & Bureau, B. (2024). Effect of Bi additive on the physical properties of Ge_2Se_3-based equichalcogenide glasses and thin films. *ACS Applied Electronic Materials, 6*(4), 2720–2727. https://doi.org/10.1021/acsaelm.4c00263

[20] Popescu, M. (2000). *Non-crystalline chalcogenides.* New York, NY: Kluwer Academic Publishers. https://doi.org/10.1007/0-306-47129-9

[21] Golovchak, R., Plummer, J., Kovalskiy, A., Holovchak, Y., Ignatova, T., Nowlin, K., Trofe, A., Shpotyuk, Y., Boussard-Pledel, C. & Bureau, B. (2022). Broadband photosensitive medium based on amorphous equichalcogenides. *ACS Applied Electronic Materials, 4*(11), 5397–5405. https://doi.org/10.1021/acsaelm.2c01075

[22] Golovchak, R., Shpotyuk, O. & Kovalskiy, A. (2023). High-resolution XPS for determining the chemical order in chalcogenide network glasses. *Journal of Non-Crystalline Solids: X, 18,* 100188. https://doi.org/10.1016/j.nocx.2023.100188

ЕЛЕКТРОННІ ВЛАСТИВОСТІ СКЛА As-Se-Te, ЛЕГОВАНОГО Ga

Ярослав Шпотюк[1,*], Адам Інграм[2], Андрій Лучечко[1],
Дмитро Слободзян[1], Маркіян Кушлик[1], Олег Кравець[1],
Михайло Шпотюк[1], Роман Головчак[3]
[1]Кафедра сенсорної та напівпровідникової електроніки,
Львівський національний університет імені Івана Франка,
вул. Тарнавського, 107, м. Львів, 79017, Україна
[2]Кафедра фізики, Політехніка Опольська,
вул. Озімська, 75, м. Ополе, 45370, Польща
[3]Кафедра фізики, інженерії та астрономії, Державний університет Остіна Пі,
м. Кларксвілл, TN 37044, США

АНОТАЦІЯ

Вступ. Система As-Se-Te привертає значну увагу, оскільки ці сорти халькогенідного скла наділені унікальними напівпровідниковими та оптичними властивостями. Широка прозорість в інфрачервоному діапазоні, нелінійність та простота формування роблять ці матеріали перспективними кандидатами для електронних і фотонних застосувань. Однак розчинність рідкісноземельних іонів у халькогенідних матрицях загалом є низькою, що обмежує їх практичне використання. Додавання Ga, як відомо, покращує розчинність рідкісноземельних іонів, проте власні електричні характеристики скла As-Se-Te, легованого Ga, залишаються переважно недослідженими.

Матеріали та методи. Досліджено композиції халькогенідного скла системи As-Se-Te леговані Ga. Зразки були отримані з високочистих прекурсорів методом плавлення з подальшим охолодженням. Оптичні, структурні та електронні властивості досліджених зразків були вивчені за допомогою високороздільної Х-променевої фотоелектронної спектроскопії (XPS), імпедансної спектроскопії та оптичної спектроскопії.

Результати. Введення як Ga, так і Te призводить до зменшення ширини забороненої зони порівняно з бінарним склом As_2Se_3. Спектри валентної зони, отримані методом рентгенівської фотоелектронної спектроскопії для досліджених матеріалів демонструють характерні особливості, схожі на інші бінарні та тернарні халькогеніди, що відображає внесок електронних станів Se, Te, As та Ga. Ці результати вказують на те, що електронна структура сильно визначається зв'язками халькоген–As(Ga), що впливає на густину станів валентної зони та пов'язані з дефектами. Температурно-залежна електропровідність постійного струму демонструє кілька механізмів провідності. Введення Ga знижує енергію активації при високих температурах через модифікацію процесу провідності, тоді як зразки, що містять Te, демонструють ще вищі значення енергії активації, що вказує на внесок механізмів стрибкоподібної провідності та дефектних станів.

Висновки. Вплив Ga та Te на оптичні та електронні властивості халькогенідного скла на основі As_2Se_3 досліджувався за допомогою оптичної та імпедансної спектроскопії. Показано, що електронні властивості композицій скла As-Se-Te, модифікованого Ga мають важливе значення для їх потенційного використання в інтегрованих оптоелектронних платформах. Отримані результати корелюють зі структурою валентної зони цих матеріалів, визначеною за допомогою рентгенівської фотоелектронної спектроскопії.

Ключові слова: халькогенідне скло, електропровідність постійного струму, заборонена зона, температурна залежність.

Received / Одержано	Revised / Доопрацьовано	Accepted / Прийнято	Published / Опубліковано
26 August, 2025	08 September, 2025	12 September, 2025	31 October, 2025