



**B. O. Seredyuk<sup>1</sup>, O. R. Dveriy<sup>1</sup>, F. O. Ivashchyshyn<sup>2</sup>**

<sup>1</sup> Hetman Petro Sahaidachnyi National Army Academy, Lviv, Ukraine

<sup>2</sup> Lviv Polytechnic National University, Lviv, Ukraine

## STUDIES OF THE ELECTRICAL, MAGNETIC AND STRUCTURAL PROPERTIES OF A3B6 TYPE LAYERED SEMICONDUCTORS INTERCALATED BY METALS WITH REGARD TO THEIR MILITARY APPLICATIONS

The authors have outlined the application of magnetoresistive structures based on semiconductor crystals of InSe for high precision measurement of the magnetic field. We have also described some possibilities of using magnetic field sensors based on InSe structures for revealing the armour military vehicles. The impact of metal impurities on the layered structure of the semiconductor material as referred to the strong covalent bond within the layers as well as the weak van-der-Waals bond in the interlayer space is studied. Bode diagrams for InSe crystals with the impurities of nickel at different temperatures ranging from liquid nitrogen to room temperature are analyzed. Topological images of crystal surface obtained by using atomic force microscopy confirmed the layer structure of nickel-intercalated InSe. Impedance spectroscopy measurements in the frequency range of  $10^{-3} \div 10^6$  Hz were carried out using a measuring complex "AUTOLAB" by the company "ECO CHEMIE". Magnetoresistive structures can both provide a Coulomb blockade of the electric current, and create conditions for the emergence of new unique magnetic properties that serve as the basis for new approaches to technology issues such as information carriers. In particular, the giant magnetoresistive effect in nanostructures with alternating semiconductor and metal layers offers the prospect of a radical restructuring of materials technology – development of information carriers and the creation of highly effective quantum computers. Structures with alternating layers of semiconductor and metal provide the fundamental possibility to control the magnetic properties. These structures have sharp anisotropy of magnetic susceptibility. Thus, the investigated semiconductor crystals with impurities of 3 d-elements can extend the functionality of modern magnetic sensors designed to detect heavy armor.

**Keywords:** layered semiconductor; impedance; Bode diagrams; intercalation.

**Introduction.** Magnetic sensors are often used for security and military applications such as detection, discrimination and localization of ferromagnetic and conducting objects, navigation, position tracking and antitheft systems (Ripka, 2001). Magnetic sensors are key elements in many security and military systems. Traditional sensors such as fluxgates, induction coils and resonance magnetometers are complemented by new sensor types such as AMR (Anisotropic MagnetoResistors), GMR (Giant Magneto-Resistance), SDT (Spin-Dependent Tunneling) and GMI (Giant Magneto-Impedance) sensors (Ripka & Janosek, 2010).

InSe is a typical layered semiconductor material from A3B6 group, that can be used for optical detectors in visible and near infrared spectrum region. In quantum electronics these structures can be used for the creation of the high-efficient photovoltaic converters, gas sensors and thermoelectric transducer, as well as the effective THz laser radiation sources (Oyama et al., 2008).

InSe structure is characterized by the fact that it can be viewed as quasi two-dimensional (2D) (Ripka, 2001). In-Se atoms form layers with strong covalent bond, while interlayer space is filled with a weak Van der Waals bond, so processes across the layers can be viewed as a perturbation to the ones along the layers. This leads to strong anisotropy of the properties of these structures (Shabatura et al., 2012; Seredyuk, 2014).

The discovery of single-atomic layer graphene (Novoselov et al., 2000) has led to a surge of interest in other anisotropic crystals with strong in-plane bonds and weak, van der Waals-like, inter-layer coupling. A variety of two-dimensional (2D) crystals with high crystalline quality and stable properties under ambient conditions have been investigated recently. Interest in these systems is motivated partly by the possibility of combining them with graphene to create 2D electronic devices, e.g., field effect transistors with high on-off switching ratios and memory cells (Mudd & Svatek, 2013).

### Інформація про авторів:

**Середюк Богдан Олександрович**, канд. фіз.-мат. наук, доцент, професор кафедри електромеханіки та електроніки.

Email: b.seredyuk@gmail.com

**Дверій Остап Романович**, викладач кафедри електромеханіки та електроніки. Email: o.dverij@gmail.com

**Іващишин Федір Олегович**, канд. техн. наук, мол. наук. співробітник кафедри прикладної фізики і наноматеріалознавства.

Email: fivash@i.ua

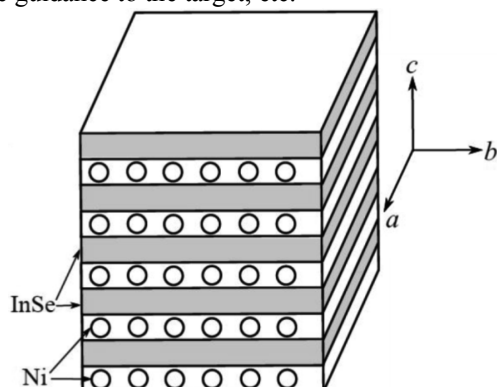
**Цитування за ДСТУ:** Середюк Б. О., Дверій О. Р., Іващишин Ф. О. Дослідження електричних, магнітних і структурних властивостей шаруватих напівпровідникових кристалів типу АЗВ6, інтеркальованих металами з огляду на їх військове застосування. Науковий вісник НЛТУ України. 2017. Вип. 27(10). С. 117–121.

**Citation APA:** Seredyuk, B. O., Dveriy, O. R., & Ivashchyshyn, F. O. (2017). Studies of the Electrical, Magnetic and Structural Properties of A3B6 Type Layered Semiconductors Intercalated by Metals with Regard to Their Military Applications. *Scientific Bulletin of UNFU*, 27(10), 117–121. <https://doi.org/10.15421/40271022>

In recent work these materials were shown to possess magnetoresistive properties and were proved to be useful for magnetic sensors (Shabatura et al., 2012; Seredyuk, 2014; Seredyuk, 2016; Seredyuk, 2017). Nowadays sensitive magnetic sensors are used in many technical systems, including modern anti-tank missiles to identify the center of the target area and a minimal armor region. Materials based on magnetoresistive structures are resistant to extreme temperatures, and ionizing radiation, so they are promising for use in guidance systems of modern microprocessor warheads (Dalichaouch, Czipott & Perry, 2001).

**Basic statements.** Magnetic sensors numerically register these perturbations (anomalies) of the background magnetic field of the Earth, and modern methods of digital processing of analog signals allow a relatively accurate determination of the mass, direction and speed of the above mentioned objects (Dalichaouch, Czipott & Perry, 2001). Over the past 30 years magnetoresistive structures boost their share role on sensor technology sector of the market of weaponry.

Magnetoresistive structures – objects that have the ability to alter their current-voltage characteristics depending on changes in the external magnetic field. Sensors based on magneto-resistive structures are highly sensitive to the magnetic field fluctuations ( $10^{-15}$  T at temperatures of liquid helium, and  $10^{-13}$  T at room temperature) (Lenz & Edelstein, 2006). This property is used in a wide field of military technologies, such as: navigation, detection of submarines, missile guidance to the target, etc.



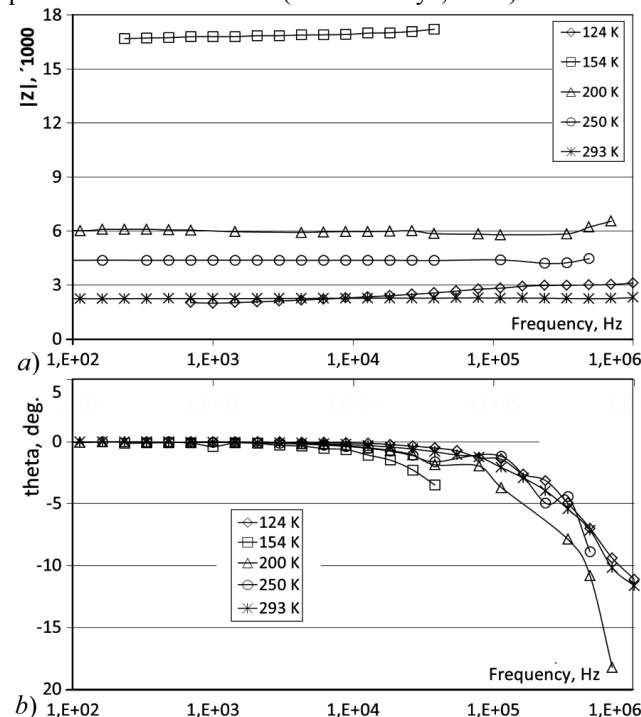
**Figure 1.** InSe structure ( $a=b=4,002$  Å,  $c=24,946$  Å) intercalated with Ni

InSe is one of the materials susceptible to a giant magnetoresistive effect (Phan & Peng, 2008) which makes it useful for magnetic sensors. The explanation of this phenomenon is based on a quantum-mechanical theory and is thoroughly described in.

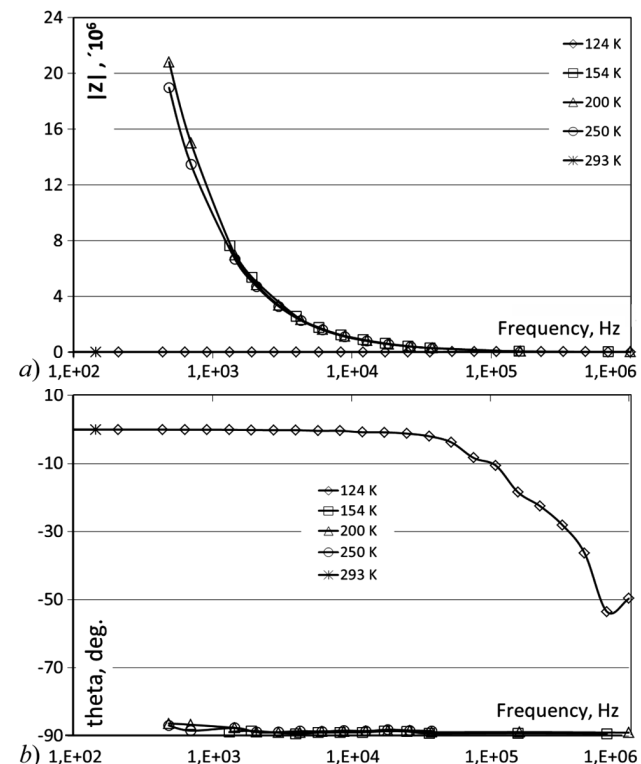
**Presenting main material.** The unique possibilities of change of the ferromagnetic properties of a hybrid system ferromagnetic-semiconductor by the optical and electrical methods cause today heightened interest (Nikitin, 2004). Such changes may be used, in particular, at making of the modern functional units of spintronics. As the effect of the influence of semiconductor on a ferromagnetic is more marked for the thin ferromagnetic film there is actual a problem of reception of the semiconductor structures with minimally possible thickness alternating magnetoactive layers (Pokladok et al., 2008).

Introduction (intercalation) of different by their properties foreign atoms, in particular metallic atoms of the iron transition group into the structure of the layered crystal expands the range of new compounds with unique properties.

The appearance of even a small concentration of magnetic impurities in the InSe crystal may significantly affect the electrical, magnetic and optical properties of the crystal. Lattice, in its turn, will affect the magnetic moment of the intercalant leading to anomalous kinetic and magnetic properties of such structures (Zakharchenya, 2005).



**Figure 2.** Bode diagrams for pure InSe at different temperatures



**Figure 3.** Bode diagrams for InSe with Ni (5 %) at different temperatures

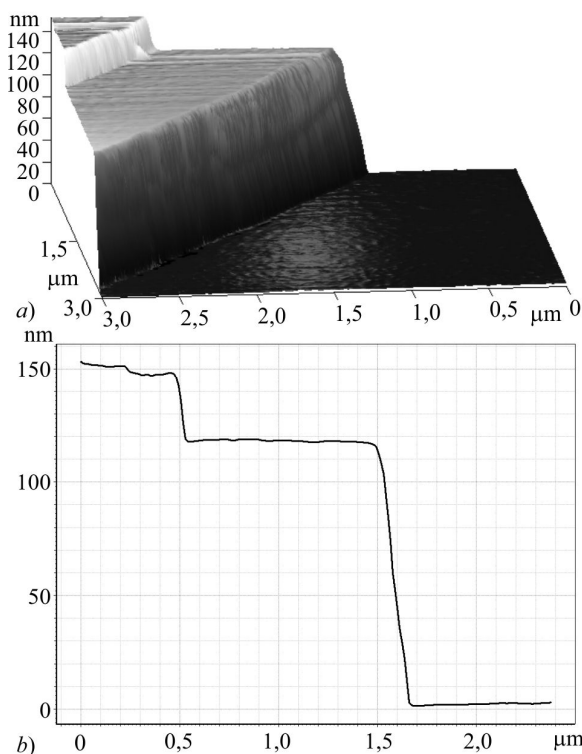
For example, the introduction of the element of 3d-iron group in the  $\text{TiSe}_2$  matrix leads to the formation of Ti-M-Ti covalent centers. In the case of  $\text{M}_x\text{TiSe}_2$ , (where M – metal atoms of Ni, Co, Ag) intercalation is accompanied by a decrease in the lattice constant along the anisotropy axis (Titov & Dolgoshein, 2000).

The covalent centers of In-M-In in the  $\text{Ni}_x\text{InSe}$  structure can act as traps for free charge carriers, on the one hand, and as centers of lattice distortion on the other. Since the introduction of metal atoms of 3d-iron group into the matrix of the layered semiconductor crystals significantly affects their properties, the magnetization can be assumed to be an important factor regulating the above mentioned effects under the influence of an external magnetic field (Zakharchenya, 2005; Titov & Dolgoshein, 2000). The influence of metal atoms of 3d-iron group on the matrix of semiconductor layered crystals was studied in details in (Phan & Peng, 2008). Some peculiarities of the behavior of  $\text{In}_4\text{Se}_3$  doped by metallic impurities have been discussed in (Seredyuk, 2014, 2016, 2017).

To investigate the effect of metallic impurities on the layered InSe structure Bode diagrams for: pure InSe; and InSe with Ni (5 %) are outlined in the Figures below.

To analyze the layered structure of InSe the raw data of the topological images of pure InSe surface captured by atomic force microscope (AFM) Solver P47 PRO (NT-MDT) taken from (Seredyuk, Ivashchyshyn & Kulyk, 2017) have been used. The measurements have been done in contact mode employing Si-type cantilevers with a tip rounding radius of 10 nm. To obtain the Figures 4-7 NOVA R13.6.0 software was used to process the raw data published in.

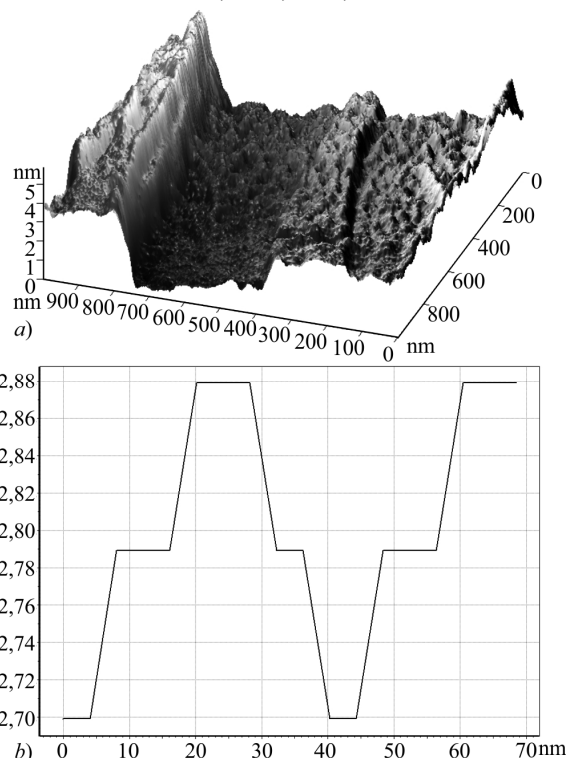
3D AFM image of the  $3\text{ }\mu\text{m} \times 3\text{ }\mu\text{m}$  section of InSe acquired with the pin step of 10,6 nm and 0,09 nm resolution in the direction perpendicular to the shear planes is shown in Fig. 4a. Cross section of the shear planes perpendicular to the layers of InSe indicating step heights of two adjacent layers is shown in Fig. 4b.



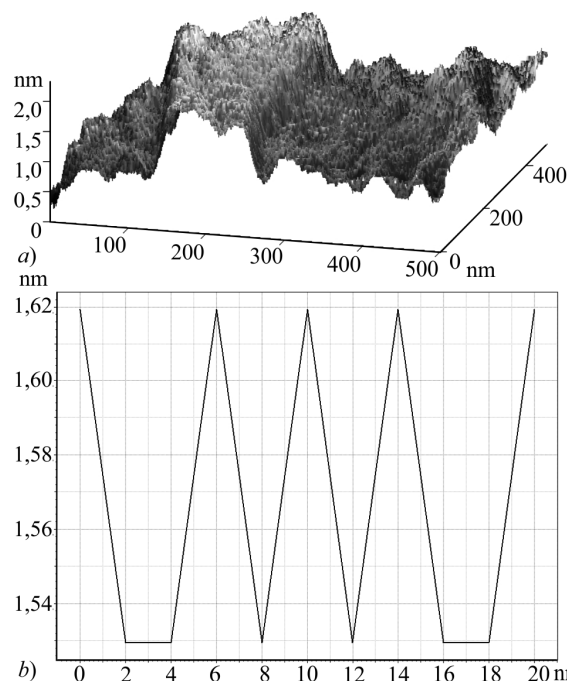
**Figure 4.** a) 3D AFM image of the  $3\text{ }\mu\text{m} \times 3\text{ }\mu\text{m}$  section of InSe layered structure; b) Cross sections of InSe adjacent layers

As it is shown by Fig. 4 b InSe shear planes are smooth in the scale of 2 nm (perpendicular to the layers). The obtained image of the layer steps is not perpendicular to the shear planes, which is caused by the specific geometry of the AFM probe needle. To study the InSe surface experiments

with a smaller step size of the AFM probe needle have been carried out (Fig. 5, 6). Resolution in the direction perpendicular to the shear planes was 0,09 nm which is quite sufficient for the given measurements taking into account the size of the InSe unit cell of  $0,4 \times 0,4 \times 2,5\text{ nm}^3$ .



**Figure 5.** a) 3D AFM image of the  $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$  section of InSe with the pin step of 3,75 nm and 0,09 nm resolution in the direction perpendicular to the shear planes; b) Local cross sections of InSe adjacent layers



**Figure 6.** a) 3D AFM image of the  $500\text{ nm} \times 500\text{ nm}$  section of InSe with the pin step of 1,86 nm and 0,09 nm resolution in the direction perpendicular to the shear planes; b) Local cross sections of InSe adjacent layers

**Conclusions.** Bode diagrams demonstrate that the presence of Ni makes considerable changes to total impedance and dielectric loss angle of InSe structure. This may be due to the traps for charge carriers introduced by the guest Ni



which makes  $\text{Re } Z$  and  $\text{Im } Z$  susceptible of the frequency change. Temperature is shown to be a significant factor for affecting the Bode diagrams. AFM images of pure InSe confirm its layered structure with the obtained single layer thickness of about 0,7 nm. A step size of the AFM probe needle has been proved to be an important factor for layer surface analysis.

## Перелік використаних джерел

- Dalichaouch, Y., Czipott, P., & Perry, A. (2001). Magnetic sensors for battlefield applications. *Proc. SPIE*, 4393, 129–134. <https://doi.org/10.1117/12.441262>
- Lenz, J., & Edelstein, A. S. (2006). Magnetic sensors and their applications. *IEEE Sens. J.*, 6, 631–649. <https://doi.org/10.1109/JSEN.2006.874493>
- Mudd, G. W., & Svatek, S. A. (2013). Tuning the Bandgap of Exfoliated InSe Nanosheets by Quantum Confinement. *Adv. Mater.*, 25, 5714–718. <https://doi.org/10.1002/adma.201302616>
- Nikitin, S. A. (2004). *Soros. journ. education*, 8(2), 92–95.
- Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V., & Firsov, A. A. (2000). Electric field effect in atomically thin carbon films. *Science*, 306–666. <https://doi.org/10.1126/science.1102896>
- Oyama, Y., Tanabe, T., Sato, F., Kenmochi, A., Nishizawa, J., Sasaki, T., Suto, K., & Cryst, J. (2008). Liquid-phase epitaxy of GaSe and potential application for wide frequency-tunable coherent terahertz-wave generation. *J. Cryst. Grow.*, 310, 1923–1928.
- Phan, M. H., & Peng, H. X. (2008). Giant magnetoresistance materials: Fundamentals and applications. *Progress in Materials Science*, 53, 323–420. <https://doi.org/10.1016/j.pmatsci.2007.05.003>
- Pokladok, N. T., Grygorchak, I. I., Lukiyanets, B. A., & Popovych, D. I. (2008). Ripetsky peculiarities of magnetoresistance in single

- crystals in solid and gas, laser intercalated by chrome. *Optyko-elektronni informatsiino-enerhetychni tekhnologii*, 1, 114–118.
- Ripka, P. (2001). Security applications of magnetic sensors. *Journal of Physics Conference Series* 06/2013; 450(1). <https://doi.org/10.1088/1742-6596/450/1/012001>
- Ripka, P., & Janosek, M. (2010). Advances in Magnetic Field Sensors. *IEEE Sens. J.* 10. Issue: 6, 1108–1116. <https://doi.org/10.1109/JSEN.2010.2043429>
- Seredyuk, B. O. (2014). A study of the kinetic properties of nanostructured intercalates of  $\text{Ag}_x\text{In}_4\text{Se}_3$  aimed at the creation of photodetectors. *Military-technical book*, 2(11), 52–55.
- Seredyuk, B. O. (2016). Analysis of electrical and magnetic properties of semiconductor crystals of Inse type intercalated by metals due to their military applications. *Military-technical book*, 14, 50–53. [in Ukrainian].
- Seredyuk, B. O. (2017). Analysis of electrical and magnetic properties of semiconductor crystals of inse type intercalated by metals due to their military applications. *Military-technical book*, 16, 21–24.
- Seredyuk, B. O., Ivashchyshyn, F. O., Kulyk, B. Ya. (2017). Analysis of the electrical, magnetic and structural properties of A3B6 type layered semiconductor crystals intercalated with metals with reference to their military applications. *Military-technical book. in print.*, 3(5), 23–31.
- Shabatura, Yu. V., Seredyuk, B. O., Korolko, S. V., & Fomenko, V. L. (2012). The prospects of military applications of magnetic sensors based on GMR effect in  $\text{Ni}_x\text{InSe}$ . *Military-technical book*, 2(7), 80–84. [in Ukrainian].
- Titov, A. N., & Dolgoshein, A. V. (2000). Phase diagrams of the intercalate materials with a polar type of carriers localization. *Solid State Physics*, 42(3), 425–427. [in Russian].
- Zakharchenya, B. P. (2005). Integrating magnetism into semiconductor electronics. *Ukrainian Physical Journal*, 175(11), 629–675. [in Ukrainian].

**Б. О. Середюк<sup>1</sup>, О. Р. Дверій<sup>1</sup>, Ф. О. Іващук<sup>2</sup>**

<sup>1</sup> Національна академія сухопутних військ ім. гетьмана Петра Сагайдачного, м. Львів, Україна  
<sup>2</sup> Національний університет "Львівська політехніка", м. Львів, Україна

## ДОСЛІДЖЕННЯ ЕЛЕКТРИЧНИХ, МАГНІТНИХ І СТРУКТУРНИХ ВЛАСТИВОСТЕЙ ШАРУВАТИХ НАПІВПРОВІДНИКОВИХ КРИСТАЛІВ ТИПУ АЗВ6, ІНТЕРКАЛЬОВАНИХ МЕТАЛАМИ З ОГЛЯДУ НА ЇХ ВІЙСЬКОВЕ ЗАСТОСУВАННЯ

Проаналізовано перспективи застосування магніторезистивних структур на основі напівпровідникових кристалів типу InSe для прецизійного вимірювання магнітного поля. Розглянуто можливість застосування сенсорів магнітного поля на основі структури InSe для виявлення важкої механізованої техніки, зокрема й військової бронетехніки. Досліджено вплив домішок металів на шарувату структуру напівпровідникового матеріалу, як на сильний ковалентний зв'язок всередині шару, так і на слабкий Ван-дер-Ваальсовий зв'язок у міжшаровому просторі. Застосовано метод імпедансної спектроскопії за частот до  $10^6$  Гц для дослідження електричних параметрів кристалів InSe. Проаналізовано діаграми Бode для бездомішкового кристалу InSe та кристалу з домішками нікелю (5 %) за різних температур – від кімнатної до температури рідкого азоту. Отримані методом атомно-силової мікроскопії топографічні знімки поверхонь бездомішкового InSe підтверджують його шарувату структуру. Магніторезистивні структури можуть не тільки забезпечувати кулонівську блокаду електричного струму, але і створювати умови для виникнення нових унікальних магнітних властивостей, які стануть основою для нових підходів у технології матеріалів – носіїв інформації. Зокрема, гігантський магніторезистивний ефект у наноструктурах з почерговими напівпровідниковими та металічними прошарками відкриває перспективу докорінної перебудови технології матеріалів – носіїв інформації і створення надвисокоєфективних квантових комп'ютерів.

**Ключові слова:** шаруватий напівпровідник; імпеданс; діаграми Бode; інтеркаляція.

**Б. О. Середюк<sup>1</sup>, О. Р. Дверій<sup>1</sup>, Ф. О. Іващук<sup>2</sup>**

<sup>1</sup> Национальная академия сухопутных войск им. гетмана Петра Сагайдачного, г. Львов, Украина  
<sup>2</sup> Национальный университет "Львовская политехника", г. Львов, Украина

## ИССЛЕДОВАНИЕ ЭЛЕКТРИЧЕСКИХ, МАГНИТНЫХ И СТРУКТУРНЫХ СВОЙСТВ СЛОИСТЫХ ПОЛУПРОВОДНИКОВЫХ КРИСТАЛЛОВ ТИПА АЗВ6, ИНТЕРКАЛИРОВАННЫХ МЕТАЛЛАМИ С ТОЧКИ ЗРЕНИЯ ИХ ВОЕННОГО ПРИМЕНЕНИЯ

Выполнен анализ перспектив применения магниторезистивных структур на основе полупроводниковых кристаллов типа InSe для прецизионного измерения магнитного поля. Рассмотрена возможность применения сенсоров магнитного поля на основе структуры InSe для обнаружения тяжелой механизированной техники, в частности военной бронетехники. Исследовано влияние примесей металлов на слоистую структуру полупроводникового материала, как на сильную ковалентную связь внутри слоя, так и на слабую Ван-дер-Ваальсовую связь в межслоевом пространстве. Применен метод импедансной спектроскопии на частотах до  $10^6$  Гц для исследования электрических параметров кристаллов InSe. Проанализированы ди-

аграммы Боде для безпримесного кристалла InSe и кристалла InSe с примесями никеля (5 %) при различных температурах – от комнатной до температуры жидкого азота. Топологические снимки поверхностей безпримесного InSe с использованием методики атомно-силовой микроскопии подтверждают его слоистую структуру. Магниторезистивные структуры могут не только обеспечивать кулоновскую блокаду электрического тока, но и создавать условия для возникновения новых уникальных магнитных свойств, которые послужат основой для новых подходов в технологии материалов – носителей информации. В частности, гигантский магниторезистивный эффект в наноструктурах с последовательными полупроводниковыми и металлическими слоями открывает перспективу коренной перестройки технологии материалов – носителей информации и создание сверх высокоэффективных квантовых компьютеров.

**Ключевые слова:** слоистый полупроводник; импеданс; диаграммы Боде; интеркаляция.