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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 $10^{-3} \div 106$ 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 Tunelling) 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., 1923, 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).

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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.

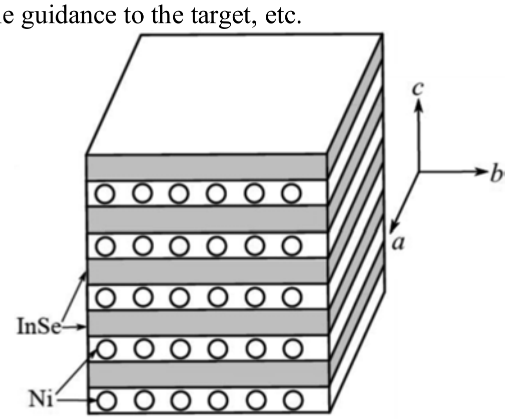

Figure 1. InSe structure (a=b=4,002 Å, c=24,946 Å) intercalated with Ni

InSe is one of the materials susceptible to a giant magneto resistive 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 throroughly 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).

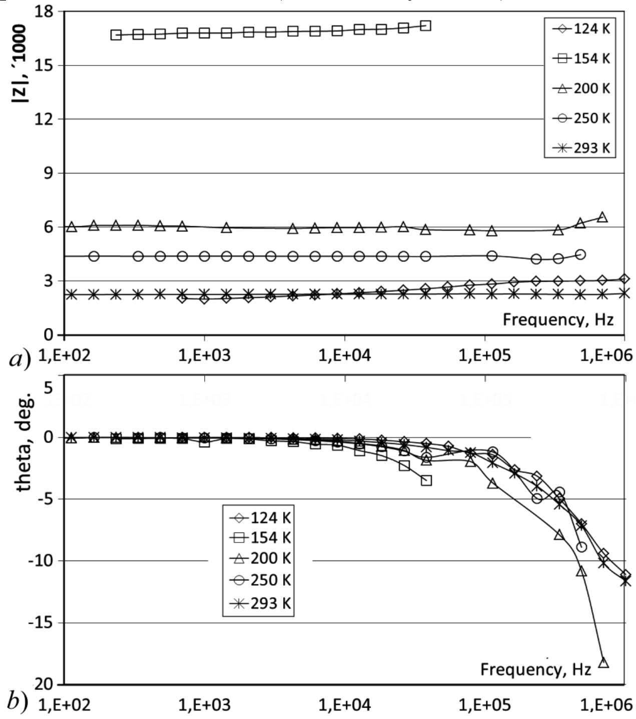

Figure 2. Bode diagrams for pure InSe at different temperatures

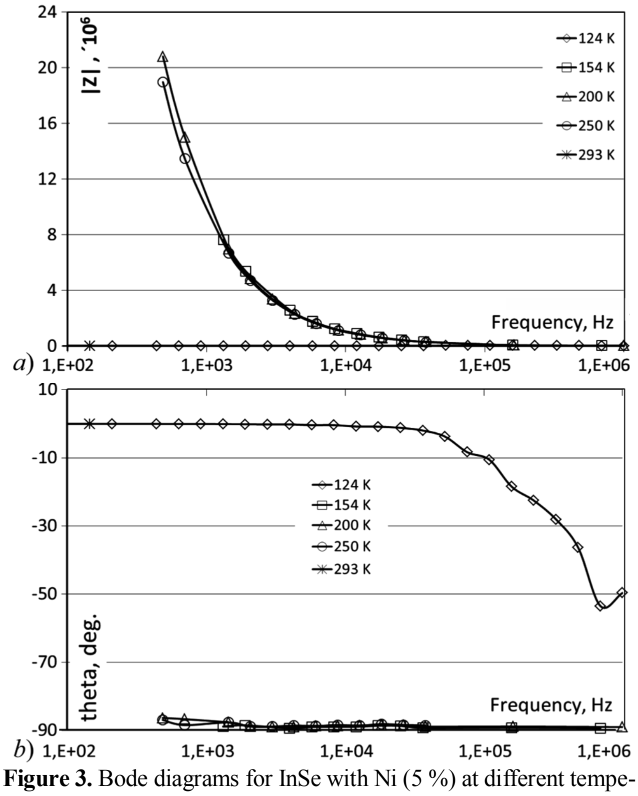

Figure 3. Bode diagrams for InSe with Ni (5 %) at different temperatures

For example, the introduction of the element of 3d-iron group in the $TiSe_2$ matrix leads to the formation of Ti-M-Ti covalent centers. In the case of M_xTiSe_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 Ni_xInSe 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 3 d-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 3 d-iron group on the matrix of semiconductor layered crystals was studied in details in (Phan & Peng, 2008). Some peculiarities of the behavior of In_4Se_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, 2007) 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 μm × 3 μm 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. 4*a*. Cross section of the shear planes perpendicular to the layers of InSe indicating step heights of two adjacent layers is shown in Fig. 4*b*.

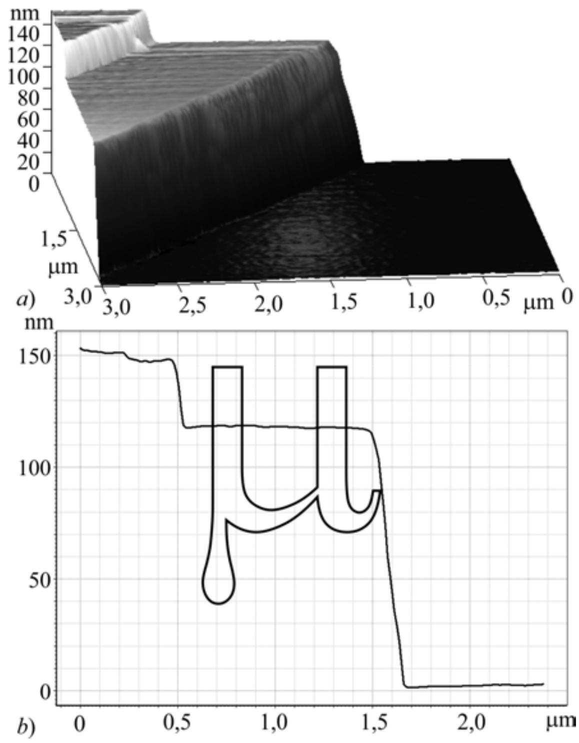

Figure 4. a) 3D AFM image of the 3 μm × 3 μm section of InSe layered structure; b) Cross sections of InSe adjacent layers

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 × 0,4 × 2,5 nm^3.

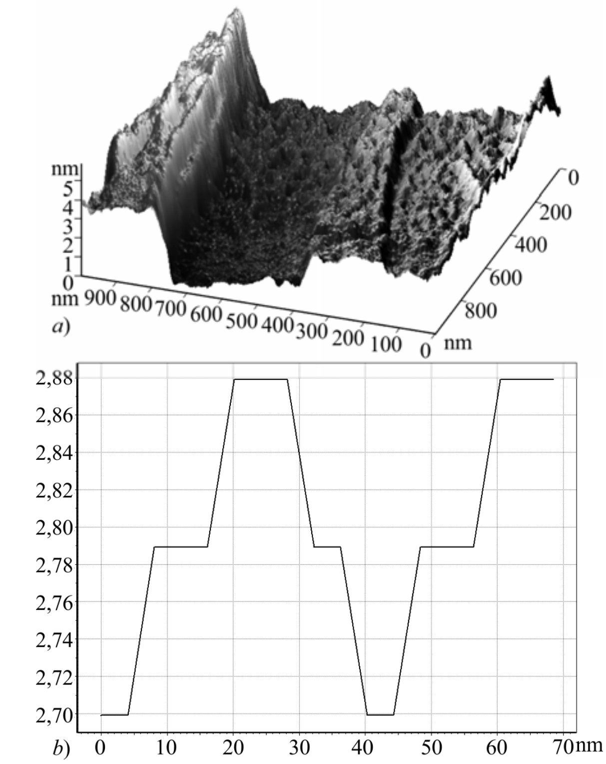

Figure 5. a) 3D AFM image of the 1 μm × 1 μm section of InSe with the pin step of 3,75 nm and 0,09 nm resolution in the direction perpendicular to the shear planes; b) Local cross sections of InSe adjacent layers

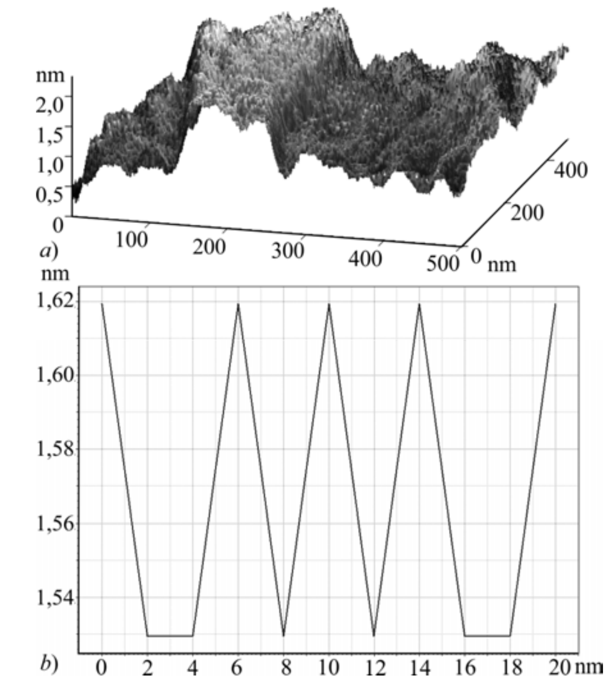

Figure 6. a) 3D AFM image of the 500 nm × 500 nm section of InSe with the pin step of 1,86 nm and 0,09 nm resolution in the direction perpendicular to the shear planes; b) Local cross sections of InSe adjacent layers

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 Re Z and 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.

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ДОСЛІДЖЕННЯ ЕЛЕКТРИЧНИХ, МАГНІТНИХ І СТРУКТУРНИХ ВЛАСТИВОСТЕЙ ШАРУВАТИХ НАПІВПРОВІДНИКОВИХ КРИСТАЛІВ ТИПУ А3В6, 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 Боде для бездомішкового кристалу InSe та кристалу з домішками нікелю (5 %) за різних температур – від кімнатної до температури рідкого азоту. Отримані методом атомно-силової мікроскопії топологічні 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 надвисокоефективних квантових комп'ютерів.

Ключові слова: шаруватий напівпровідник; імпеданс; діаграми Боде; інтеркаляція.

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ИССЛЕДОВАНИЕ ЭЛЕКТРИЧЕСКИХ, МАГНИТНЫХ И СТРУКТУРНЫХ СВОЙСТВ СЛОИСТЫХ ПОЛУПРОВОДНИКОВЫХ КРИСТАЛЛОВ ТИПА А3В6, 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 диаграммы 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.