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INFLUENCE OF THE METALLIC IMPURITIES IN A3B6 TYPE LAYERED SEMICONDUCTORS ON THEIR ELECTRICAL, MAGNETIC AND STRUCTURAL PROPERTIES

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The applications of magnetoresistive structures based on semiconductor crystals of InSe for high precision measurement of the magnetic field are outlined in this article. Possibilities of using magnetic field sensors based on InSe structures for revealing the armour military vehicles are discussed. 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 crystal 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 layered structure of nickel-intercalated InSe.

Keywords: layered semiconductor, impedance, Bode diagrams, intercalation.

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 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. Проаналізовано діаграми Боде для кристала InSe з домішками нікелю за різних температур – від кімнатної до температури рідкого азоту. Топологічні знімки поверхонь InSe з використанням методики атомно-силової спектроскопії підтверджують його шарувату структуру.

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

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 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. Проанализированы диаграммы Боде для кристалла InSe с примесями никеля при различных температурах – от комнатной до температуры жидкого азота. Топологические снимки поверхностей InSe с использованием методики атомно-силовой спектроскопии подтверждают его слоистую структуру.

Ключевые слова: слоистый полупроводник, импеданс, диаграммы Боде, интеркаляция.

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 [1]. Magnetic sensors are key elements in plenty of 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 [2].

Analysis of recent research and publications. InSe is a typical layered semiconductor material from A3B6 group, that can be employed for optical detectors in visible and near infrared spectrum region. In quantum electronics these structures can be applied for the creation of the high-efficient photovoltaic converters, gas sensors and thermoelectric transducer, as well as the effective THz laser radiation sources [3].

InSe structure is characterized by the fact that it can be considered as quasi two-dimensional (2D) [1]. In-Se atoms form layers with strong covalent bonds, while interlayer

space is filled with a weak Van der Waals bond, so processes across the layers can be regarded as a perturbation to the ones along the layers. It leads to strong anisotropy of the properties of these structures [4, 5].

The discovery of single-atomic layer graphene [6] 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 aiming the creation of 2D electronic devices, e.g., field effect transistors with high on-off switching ratios and memory cells [7].

In recent work these materials were shown to possess magnetoresistive properties and were proved to be useful for magnetic sensors [4, 5, 8, 9].

Magnetoresistive structures can not only provide a Coulomb blockade of the electric current, but also create conditions for the emergence of new unique magnetic properties that serve as the basis for new approaches to technological issues – 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.

Nowadays sensitive magnetic sensors are utilized in plenty of 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 [10].

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 [10]. 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 deviations (10^{-15} T at temperatures of

liquid helium, and 10^{-13} T at room temperature) [11]. This property is applied to a wide field of military technologies, such as: navigation, detection of submarines, missile guidance to the target, etc.

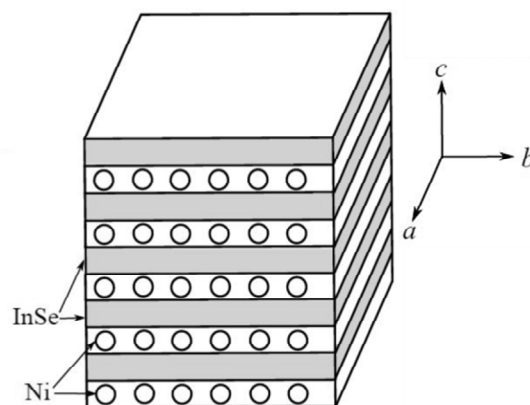


Fig. 1. InSe structure ($a=b=4,002 \text{ \AA}$, $c=24,946 \text{ \AA}$) intercalated with Ni

InSe is one of the materials susceptible to a giant magneto resistive effect [12] which makes it useful for magnetic sensors.

The explanation of this phenomenon is based on a quantum-mechanical theory and is thoroughly described in [12].

The purpose of the article. 1) To investigate the dependence of real and imaginary components of the resistivity of Ni_xInSe structure (Fig. 1) as a function of temperatures and nickel content x . 2) To analyze the impact of metallic impurity, its concentration and temperature on the electrical, magnetic and structural properties of InSe.

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 [13]. Such changes may outline the basis, in particular, for 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 arises a problem of reception of the semiconductor structures with minimally possible thickness of the alternating magneto-active layers [14].

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 [15].

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 are the metal atoms of Ni, Co, Ag) intercalation is accompanied by a decrease in the lattice constant along the anisotropy axis [16].

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 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 [15, 16]. The influence of metal atoms of 3d-iron group on

the matrix of semiconductor layered crystals was studied in details in [4]. Some peculiarities of the behavior of In_4Se_3 doped by metallic impurities have been discussed in [5, 8, 9]. 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".

To investigate the effect of metallic impurities on the layered InSe structure Bode diagrams for: pure InSe; and InSe with Ni (3 %) are outlined in the Fig. below.

To analyze the layered structure of InSe the topological images of pure InSe surface were captured by atomic force microscope (AFM) Solver P47 PRO (NT-MDT). The measurements have been done in contact mode employing Si-type cantilevers with a tip rounding radius of 10 nm.

3D AFM image of the $2,5 \mu\text{m} \times 2,5 \mu\text{m}$ section of InSe acquired with the pin step of 17,7 nm and 0,09 nm resolution in the direction perpendicular to the shear planes is demonstrated in Fig. 4a. Cross section of the shear planes perpendicular to the layers of InSe indicating step heights of two adjacent layers is presented in Fig. 4b.

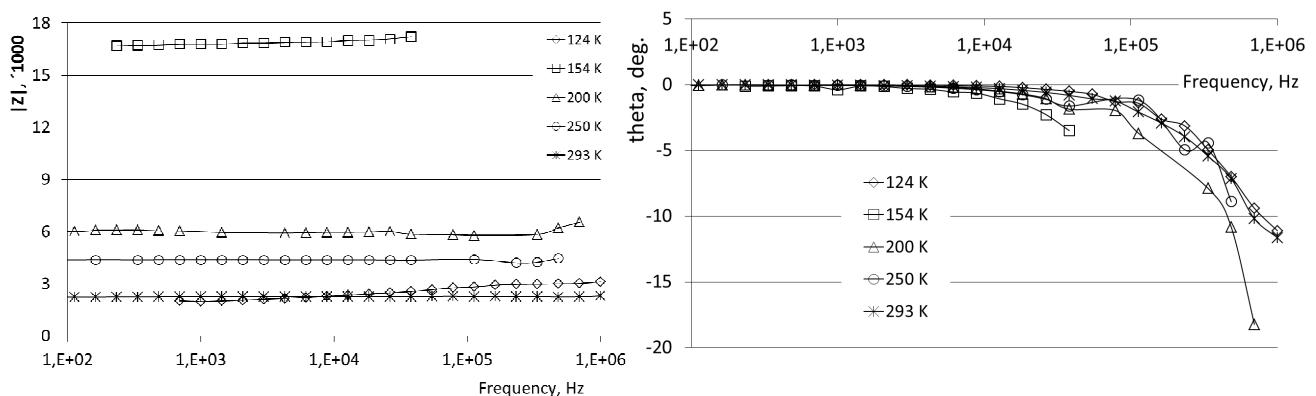


Fig. 2. Bode diagrams for pure InSe at different temperatures

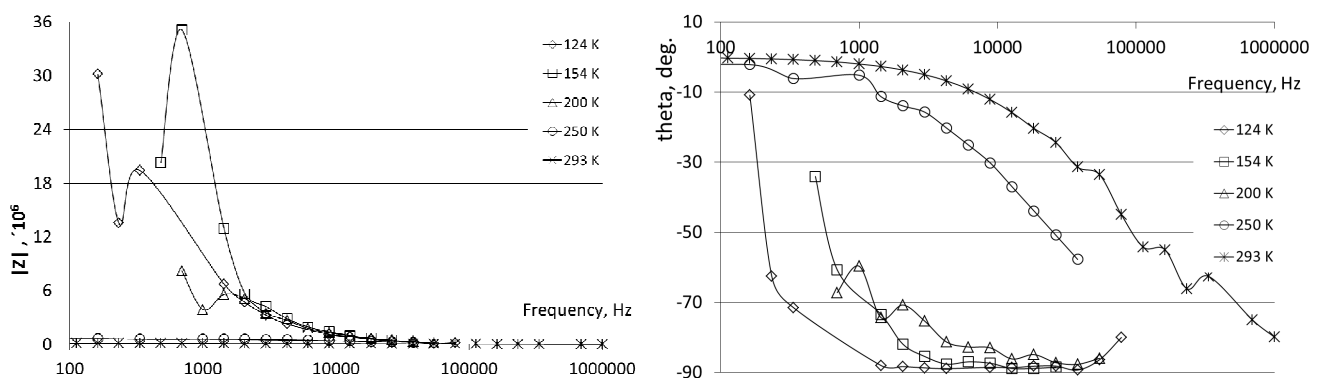


Fig. 3. Bode diagrams for InSe with Ni (3 %) at different temperatures

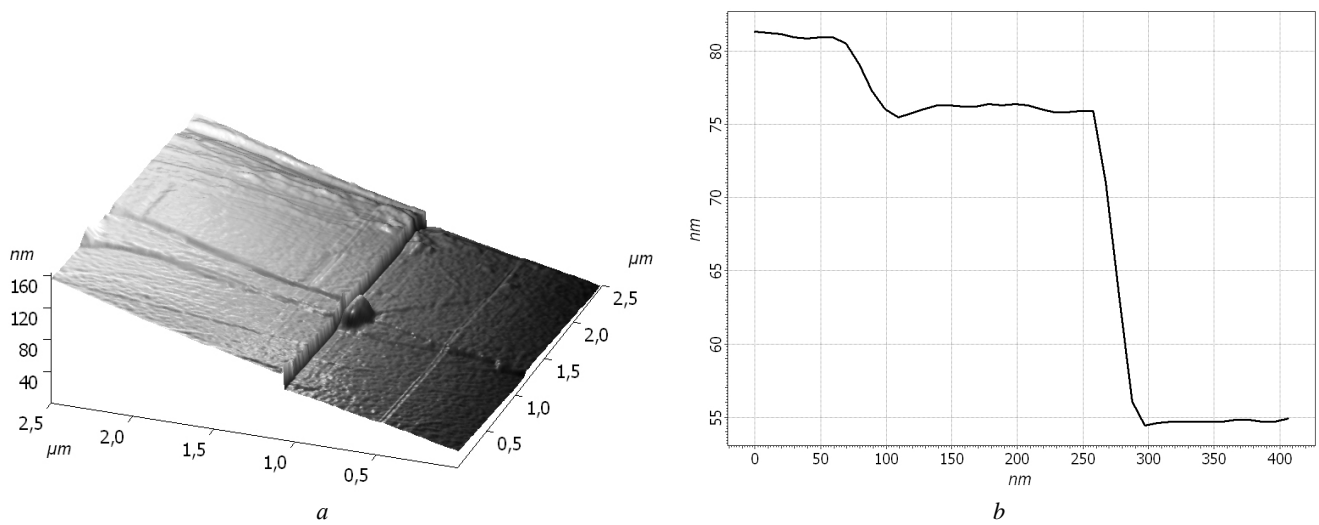


Fig. 4. 3D AFM image of the $2.5 \mu\text{m} \times 2.5 \mu\text{m}$ section of InSe layered structure (a); cross sections of InSe adjacent layers (b)

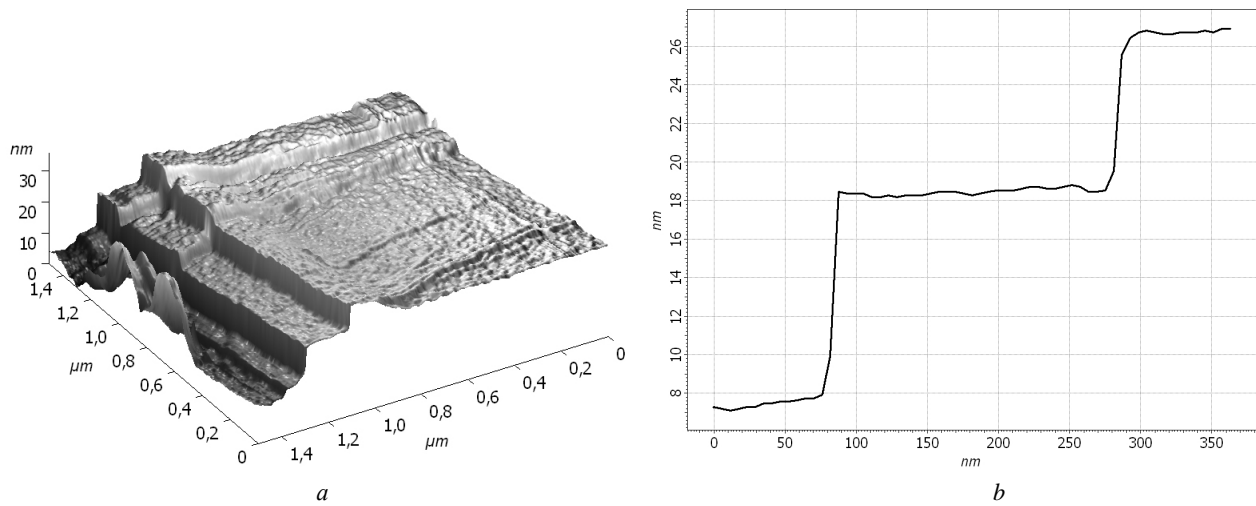


Fig. 5. 3D AFM image of the $1.5 \mu\text{m} \times 1.5 \mu\text{m}$ section of InSe with the pin step of 5,30 nm and 0,09 nm resolution in the direction perpendicular to the shear planes (a); local cross sections of InSe adjacent layers (b)

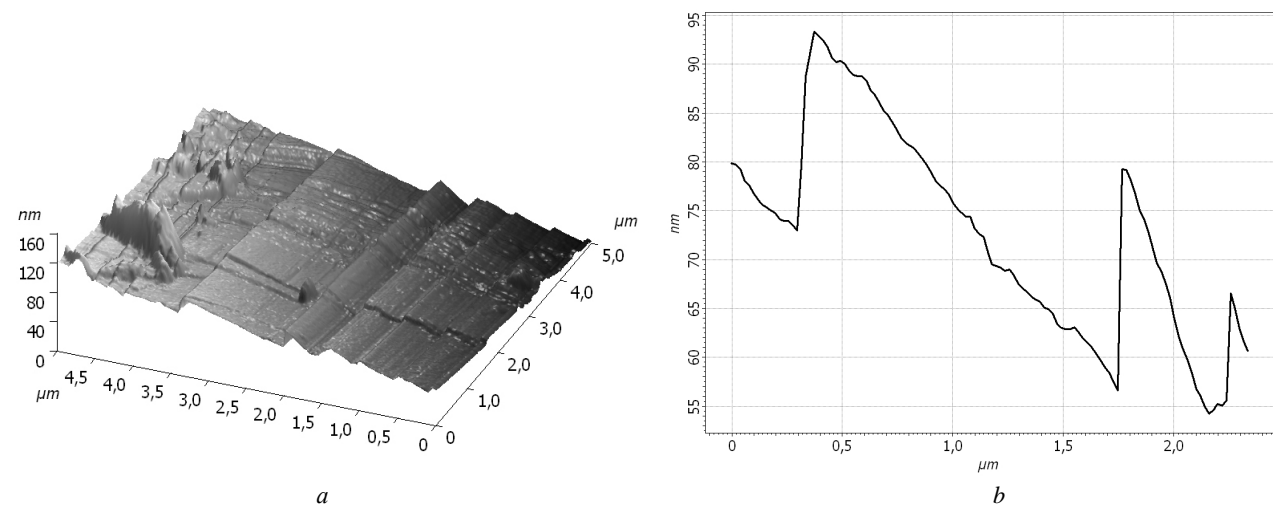


Fig. 6. 3D AFM image of the $5 \mu\text{m} \times 5 \mu\text{m}$ section of InSe with the pin step of 19,61 nm and 0,09 nm resolution in the direction perpendicular to the shear planes (a); Local cross sections of InSe adjacent layers (b)

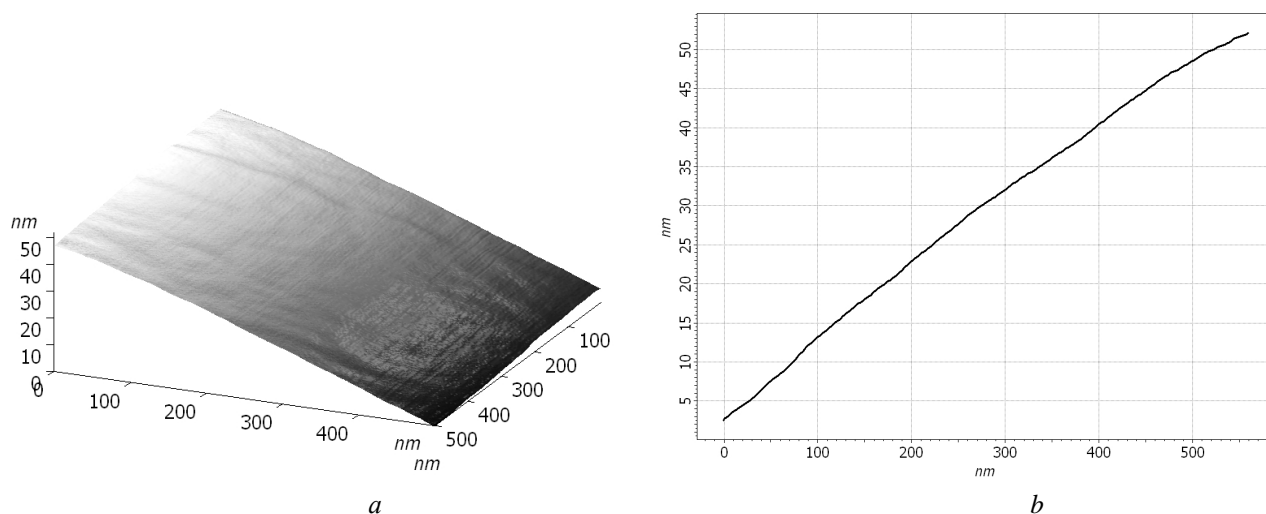


Fig. 7. 3D AFM image of the 500 nm \times 500 nm section of InSe with the pin step of 1,77 nm and 0,09 nm resolution in the direction perpendicular to the shear planes (a); Local cross sections of InSe adjacent layers (b)

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 $0,4 \times 0,4 \times 2,5 \text{ nm}^3$.

As it is shown by Fig. 4b and 5b InSe shear planes are smooth in the scale of 2nm (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.

Fig. 6 presents the sample of InSe crystal fixed at an angle between the shear and horizontal planes. As in the previous case the obtained image of the layer steps is not perpendicular to the shear planes, which is again caused by the specific geometry of the AFM probe needle. A finer step size of the AFM probe has been employed to study InSe surface which is shown in Fig. 7.

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 proved 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.

Structures with alternating layers of semiconductor and metal provide the fundamental possibility to control the

magnetic properties. A sharp anisotropy of magnetic susceptibility is inherent in these structures. The investigated semiconductor crystals with impurities of 3d-elements can extend the functionality of modern magnetic sensors designed to detect heavy armor.

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