УДК623.465.35

B. Seredyuk

Petro Sahajdachnyj Academy of Land Forces, Lviv

A STUDY OF THE KINETIC PROPERTIES OF NANOSTRUCTURED INTERCALATES OF $Ag_xIn_4Se_3$ AIMED AT THE CREATION OF PHOTODETECTORS

The prospects of application of photosensitive semiconductor nanostructures based on layered crystals In_4Se_3 are outlined in this article. The possibility of using the intercalated $Ag_xIn_4Se_3$ in the photodetectors to detect military armored vehicles is studied. The behavior of a semiconductor crystal $Ag_xIn_4Se_3$ in a uniform magnetic field using Hall effect is studied. The comparison of the behavior of pure In_4Se_3 and intercalated crystal by silver $Ag_xIn_4Se_3$ in the magnetic field and the influence of silver on the sensitivity of the crystal relative to the magnetic field disturbances are discussed in the paper. Mathematical processing of the experimental data dependence of the Hall voltage of In_4Se_3 on the magnetic field is carried out and the analytical expression of the approximating function is found.

Keywords: *nanostructures, Hall effect, intercalation, layer crystals.*

Introduction

The development of nanotechnology allows the construction of hybrid instruments and circles in which nanoscaled metals embedded into semiconductor crystals form highly integrated modules. As far as electronics is concerned it is well known [1] how to unify metallic and semiconductor materials for the implementation of the important functional properties including transistors, logic or memory devices. This functionality may be provided by photodetectors with the embedded nanoscaled electrical functional modules to ensure the "invisibility" of the device over a wide frequency range [1, 2]. These nanostructures possess by a limited number of geometrically impossible resonant optical modes, so that their hybridization and intermode interference can frequently be used in a special way.

High-performance photodetectors with a wide spectral range of optical radiation are created on the basis of semiconductor crystals with metallic inclusions [3], which is possible because of the specific nature of the forbidden energy gap E_g of the semiconductor. The problem of E_g "engineering" is carried out in various ways such as: formation of the doped hetero structures, formation of quantum dots, alteration of their composition or shape and so on.

As the most important applications of infrared systems (IRS), the following are specified: day and night reconnaissance, minefields or enemy detection, search for moving and stationary objects (targets) over large areas and determining of their location, precision weapons guidance system, automatic guidance of moving and stationary targets, communication systems, aircraft control system and so on.

Embedding of nanoscaled objects can be technologically achieved by intercalation of layered crystals with foreign atoms, in particular metals.

Layered In_4Se_3 semiconductor crystals with a band gap of 0.68 eV and a low specific conductivity (0,01-0,05 $(Ohm*sm)^{-1}$), possess by a strong ion-covalent bonding within the layers and a weak Van-der-Waals one along the axis of anisotropy (Figure 1) [4]. Consequently, these layered crystals are suitable for intercalation – introduction of different by nature foreign atoms into the Van-der-Waals gaps. In the case of the introduction of metallic impurities in the interlayer gap the conducting metal nanostructures are formed in the received intercalates [5]. Moreover, by alternating layers of semiconductor In_4Se_3 crystal and metalic mono layers of intercalant the coagulation of metal along the axis of anisotropy can be avoided. This uniform distribution of metal in the Van-der-Waals gap is achieved thanks to a specific technology of the impurities introduction into the crystal, for example during the growth of the structure [2, 4].

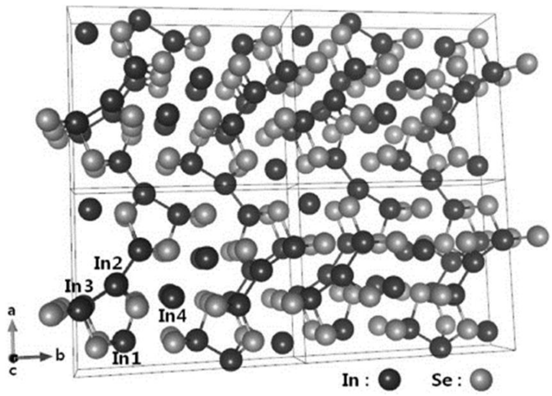

Figure 1. **The structure of In_4Se_3.**

© Б.О. Середюк

Analysis of recent research and publications

One of the research tasks in the field of infrared photodetectors is to create new technological methods of the nanostructures formation in semiconductor crystal matrix to be used as a material for optoelectronics.

Systems for scientific research should usually be of high spatial (5000x5000 cellular elements) and energy (≥ 16 bit) resolutions as well as a low level of intrinsic noise. These often include systems for the study of natural resources and environmental monitoring, although they can be applied to the second group of IRS. Plenty of these IRS do not require real time operation, ie, the output signal can be recorded on the media as film, tape, optical or magnetic memory drive rather than being displayed on the screen in the process of IRS operation. Military systems usually opearate in real time, although some of them use the "hard" media to record the observed information.

The examples of the involved military systems are: land, air and space reconnaissance, detection of various targets (including determination of the coordinates of missile launches), fire control system, convoy escort systems, navigation systems and others. The IRS used in these systems should have high spatial-resolution, provide high contrast under low illumination, a low command length (10 ... 12 bit), low level of intrinsic noise and high performance.

An ability to work in two or more spectral bands allows detecting and identifying many targets under a wide range of weather conditions, including smoke and the influence of interference or active countermeasures used by the enemy. In some systems a range, such as long-wave (8 ... 14 μ) is used mainly for target detection and the other, for example medium range (3 ... 5 μ) – for their identification. Third generation thermal imaging systems built using the semiconductor photodetectors matrix operate in the temperature range of -40 to +2000 °C. The typical resolution of modern thermal imagers – 0,1 ° C. Imaging systems are increasingly used by armed forces of the developed countries to identify manpower and equipment at any time, regardless of the possible conventional means of optical shielding used by the enemy in the visible range (camouflage). Of all of the specialized reconnaissance devices a thermal imaging device has become an important element of sighting system for armored military vehicles.

The purpose of the article

1. To investigate the prospects of application of the photosensitive nanostructures based on semiconductor layered crystals (LC) of In_4Se_3.

2. To consider the use of intercalated $Ag_xIn_4Se_3$ in the photodetectors to detect military armored vehicles.

3. To study the behavior of a semiconductor crystal of $Ag_xIn_4Se_3$ in a uniform magnetic field using the Hall effect.

4. To compare the behavior of pure and intercalated In_4Se_3 crystal by silver $Ag_xIn_4Se_3$ in a magnetic field and analyze the impact of silver on the sensitivity of the crystal relative to the magnetic field disturbances.

5. To develop a mathematical model describing the kinetic properties of $Ag_xIn_4Se_3$ based on the experimental data obtained in this work and the previously published data.

Results and Discussions

The sample layered semiconductor In_4Se_3 crystal intercalated by Ag is not an ideal resistor, since the alternating nanolayers of a conducting metal (Ag) and semiconductor (In_4Se_3) create a non uniform capacitance. Therefore, the study of these kind of structures involves determining it's current-voltage characteristics VAC on alternating current [5]. In_4Se_3 structure is characterized by the fact that it can be regarded as quasi two-dimensional. Atoms of In-Se form layers with a strong covalent bond, while the interlayer space has a weak Van-der-Waals coupling. This leads to a strong anisotropy of the properties of these structures.

Introduction (intercalation) of foreign atoms with various properties in the crystal structure may create a range of new compounds with unique properties. The appearance of even small concentrations of metal impurities in the crystal of InSe can significantly affect it's electrical, magnetic and optical properties. Lattice in turn will be affected by the intercalant, resulting in abnormal kinetic properties of such structures [4].

Since the introduction of metal atoms in the matrix of semiconductor layered crystals significantly affects their properties, it can be assumed that the uniformity of a distribution of metal in the Van-der-Waals gap is a significant factor, which regulates the above mentioned effects under external fields [4, 6].

Investigations of nanostructure formation on surfaces of the interlayer planes (100) of In_4Se_3, intercalated with silver have been carried out using the techniques of: Auger electron spectroscopy, scanning tunneling microscopy and scanning tunneling spectroscopy (STS). They all indicate that intercalant layer on plane (100) of LC is nonuniform on the local scale for Ag_x In_4Se_3 crystals, in contrast to the surfaces of specially intercalated In_4Se_3 crystals for which STS spectra in local points show the relative homogeneity of the local density of surface electronic states on the surface of study (100) [2].

The peculiarities of LC structure (Fig. 1) associated with ion-covalent bond between the atoms forming the plane of the layers and a weak Van-der-Waals bond in the direction of the axis of anisotropy, cause the specific nature of their electrical, magnetic and optical properties [4–7]. The electronic spectrum of these crystals is described by the effective mass approximation to describe the state of

© Б.О. Середюк

electrons, which are determined by a strong ion-covalent bond in the planes of layers and a weak Van-der-Waals one perpendicular to them.

Because of the absence of data in the literature on In_4Se_3 crystals intercalated by Ag the mechanism of intercalation of a similar layered semiconductor of $TlGaSe_2$ by silver will be considered. It is assumed that during intercalation of $TlGaSe_2$ by silver, Ag atoms are attached to the layers due to Ag bonds between atoms and groups of atoms Tl, GaSe [8]. The transition of electrons from the Ag atoms into the layer of $TlGaSe_2$ changes the electron density in layers and causes the occurrence of the charged groups of Ag atoms on the distances somewhat smaller than the ones of the Van-der-Waals range. As a result, covalent bridges appear between the layers and the embedded Ag atoms in the direction perpendicular to the layers, which in turn causes the non-zero polarization projection in these areas. Thus, the occurrence of covalent bridges between the layers of $Ag_xTlGaSe_2$, leads to a decrease of the dielectric constant and the polarization in the directions alongside the plane of the layer as well as its increase along the crystallographic c axis (001).

It is known [9], in pure $TlGaSe_2$ crystal a spontaneous polarization is observed only in the direction perpendicular to the c axis. In intercalated $Ag_xTlGaSe_2$ crystal a narrow dielectric hysteresis loop is observed along the c axis. At the same time a maximum value of the spontaneous polarization decreases in the direction perpendicular to the c axis.

A Hall coefficient for a pure and intercalated samples was calculated using the experimental data shown in Fig. 2 and Fig. 3 taking into account the dimensions of the samples. The dimensions of In_4Se_3 are (3,8x1,6x0,9) mm and the ones of $Ag_{0,35}In_4Se_3$ – (4,1x1,9x0,6) mm. Both samples were in the cubic form while the current was flowing along the longest facets, and the magnetic field was directed along the shortest facets perpendicular to the layers. Hall constant for In_4Se_3 is as follows: $R_0 = 3{,}7 \cdot 10^{-3}$ m^3/C, and for $Ag_{0,35}In_4Se_3$ – $R_i = 6{,}25 \cdot 10^{-3}$ m^3/C. The results obtained for the pure sample are in a good accordance with the published data [10], while the error is mainly caused by the different values of room temperatures at which measurements were carried out.

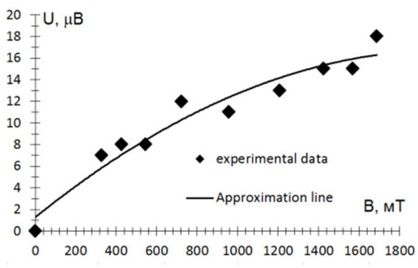

Figure 2. **Dependence of Hall voltage on the magnetic field applied perpendicular to the In_4Se_3 crystal layers (current through the sample was 5 mA)**

A dependence of Hall voltage on the magnetic field is derived from Fig. 2 using mathematical modeling methods: $U = -4 \cdot 10^{-6} B^2 + 0{,}0152 \cdot B + 1{,}2724$.

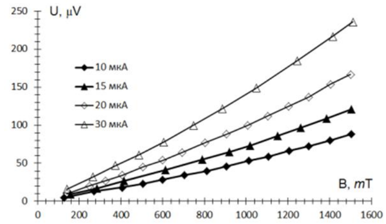

Figure 3. **Dependence of Hall voltage on the magnetic field applied perpendicular to In_4Se_3 crystal layers intercalated by silver (35 atomic %)**

Conclusions

1. It is revealed that the $Ag_{0,35}In_4Se_3$ crystal has a 70% higher sensitivity to magnetic field disturbances than In_4Se_3.

2. Structures with the alternating semiconductor and metal layers provide the possibility to control the fundamental kinetic properties. These structures have a sharp anisotropy of magnetic susceptibility. So if such a sensor is fixed on the axle and rotated with some frequency (like a radar) one can monitor the speed and direction of the armored military vehicles.

3. Semiconductor crystals doped with metals can extend the functionality of modern magnetic sensors designed to reveal heavy armored military vehicles.

Refferrences

1. Fan P. An invisible metal–semiconductor photodetector / P. Fan, U.K. Chettiar, L.C. F Afshinmanesh, N. Engheta, M.L. Brongersma // NaturePhotonics. – 2012. – Vol. 6, – №6. – P. 380–385.

2. Halij P.V. Nanostructure investigations of (100) planes of In_4Se_3 crystals intercalated by silver / P.V. Halij, T.M. Nenchuk, A. Tsizhevskyj, P. Mazur, Ja.M. Buzhuk, I.R. Jarovets // Metallophysics and new thechnologies. – 2013. – Vol. – 35. № 8. – P. 1031–1043 (in ukrainian).

3. Bandyopadhyay S. Proposal for a spintronicfemto-Tesla magnetic field sensor / S. Bandyopadhyay, M. Cahay // Physica E: Low-dimensional Systems and Nanostructures. – 2005. – № 1-2.– P. 98–103.

4. Stakhira Y. M. Structure, phase and physical properties of the films of indium selenides / Y.M. Stakhira, V.P. Savchyn, I.M. Phetsjuh // Physics boom of Shevchenko community. – 1993. – Vol. 1. – P. 321 – 333 (in ukrainian).

5. Phan M.H. Giant magnetoimpedance materials: Fundamentals and applications / M.H. Phan, H.X. Peng // Progress in Materials Science. – 2008. – Vol. 53. – P. 323–420.

6. Bercha D.M. One-Electron States in a Layered Crystal with Covalent Bridges / D.M. Bercha, L.Yu. Kharkalis, M. Sznajder // Phys. Stat. Sol. (b). – 2002. – Vol. 229, – № 3. – P. 1371 – 1396.

7. Shabatura Yu.V. The prospects of military applications of magnetic sensors base on GMR effect in Ni_xInSe / Yu.V. Shabatura, B.O. Seredyuk, S.V. Korolko, V.L. Fomenko // Millitary-technical book. – 2012. – Vol. 2 – № 7. – P. 80–84 (in ukrainian).

8. Sardarli R.M. Segnetoelectric properties of $TlGaSe_2$ crystals intercalated by silver / R.M. Sardarli, O.A. Samedov, H.R. Safarova, I.Sh. Sadigov // FIZIKA. – 2007. – Vol. 13 – № 1. – P. 317–319 (in russian).

© Б.О. Середюк

9. Sardarly R.M. Ferroelectricity and polytypism in $TlGaSe_2$ Crystals / R.M. Sardarly, O.A. Samedov, I.Sh. Sadykhov, E.I. Mardukhaeva, T.A. Gabidov // SolidStateCommunications – 1991. – Vol.77 – №.6. – P. 453–455.

10. Sznajder M. Band structure and the model of a disorder in the In_4Se_3 crystal / M. Sznajder, D.M. Bercha, L.Yu. Kharkhalis // Opto-Electr. Rev–1997. – Vol. 5 – №2. – P.123–128.

Рецензент: д.т.н., проф. Б.І. Сокіл, начальник кафедри інженерної механіки, Академія сухопутних військ імені гетьмана Петра Сагайдачного, Львів.

ОСЛІДЖЕННЯ КІНЕТИЧНИХ ВЛАСТИВОСТЕЙ НАНОСТРУКТУРОВАНИХ ІНТЕРКАЛАТІВ $Ag_xIn_4Se_3$ З МЕТОЮ СТВОРЕННЯ ФОТОДЕТЕКТОРІВ

Б.О. Середюк

У статті проаналізовано перспективи застосування фоточутливих наноструктур на основі напівпровідникових шаруватих кристалів In_4Se_3. Розглянуто можливість застосування інтеркалатів $Ag_xIn_4Se_3$ у фотодетекторах для виявлення військової бронетехніки. Вивчено поведінку напівпровідникового кристалу $Ag_xIn_4Se_3$ в однорідному магнітному полі за допомогою ефекту Хола. В роботі наведене порівняння поведінки чистого кристалу In_4Se_3 і інтеркальованого сріблом $Ag_xIn_4Se_3$ в магнітному полі та проаналізовано вплив срібла на чутливість кристала щодо збурень магнітного поля. Проведена математична обробка експериментальних даних залежностей значення холівської напруги In_4Se_3 від індукції магнітного поля, що її обумовлює, та отримані аналітичні вирази апроксимуючої функції.

Ключові слова: *наноструктури, ефект Хола, інтеркаляція, шаруваті кристали.*

ИССЛЕДОВАНИЯ КИНЕТИЧЕСКИХ СВОЙСТВ НАНОСТРУКТУРИРОВАННЫХ ИНТЕРКАЛАТОВ $Ag_xIn_4Se_3$ С ЦЕЛЬЮ СОЗДАНИЯ ФОТОДЕТЕКТОРОВ

Б.А. Середюк

В статье проанализированы перспективы применения фоточувствительных наноструктур на основе полупроводниковых слоистых кристаллов In_4Se_3. Рассмотрена возможность применения интеркалатов $Ag_xIn_4Se_3$ в фотодетекторах для выявления военной бронетехники. Изучено поведение полупроводникового кристалла $Ag_xIn_4Se_3$ в однородном магнитном поле с помощью эффекта Холла. В работе приведено сравнение поведения чистого кристалла In_4Se_3 и интеркалированного серебром $Ag_xIn_4Se_3$ в магнитном поле и проанализировано влияние серебра на чувствительность кристалла по отношению к возмущениям магнитного поля. Проведена математическая обработка экспериментальных данных зависимостей значения напряжения Холла In_4Se_3 от индукции магнитного поля, которое ее обусловливает, и получены аналитические выражения аппроксимирующей функции.

Ключевые слова: *наноструктуры, эффект Холла, интеркаляция, слоистые кристаллы.*

© Б.О. Середюк