BRIEF OVERVIEW OF THE EPR SPECTRA OF In_4Se_3 INTERCALATED BY Cu

КОРОТКИЙ ОГЛЯД ЕПР СПЕКТРІВ In_4Se_3 ІНТЕРКАЛЬОВАНИХ Cu

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Анотація. Досліджено електричні та магнітні властивості In_4Se_3, інтеркальованих міддю за допомогою ЕПР спектрів. Розглянуто можливості використання сенсорів магнітного поля на основі структур InSe для виявлення броньованих військових транспортних засобів. Досліджено вплив металевих домішок на шарувату структуру напівпровідникового матеріалу щодо сильного ковалентного зв'язку всередині шарів, а також слабкого ван-дер-ваальсового зв'язку в міжшаровому просторі. Проаналізовано спектри ЕПР для кристала In_4Se_3 з домішками Cu за кімнатної температури. Спектри ЕПР показують, що наявність Cu вносить істотні зміни в структуру In_4Se_3. Це може бути пов'язано з потряплянням вільних носіїв заряду в пастки, введені гостьовим Cu, які впливають на неспарені електрони, пов'язані з атомами In або Se. Встановлено, що вміст Cu є важливим фактором впливу на відгук структури InSe до перехресних електромагнітного та магнітних полів у спектрах ЕПР. g фактор неспарених електронів у $Ni_xIn_4Se_3$ згідно зі спектральними характеристиками, набував значення 2,017. Це значення, як з'ясовано, лежить у межах 1 % точності щодо стандартного значення $g_e = 2{,}0023$. Наявність Cu призводить до тенденції висхідного характеру спектра ЕПР, збільшуючи відгук системи зі зростанням магніного поля. Оскільки наявність Cu спричиняє специфічні (не зовсім зрозумілі) пікові значення у спектрах ЕПР, в околі значень 3400 Гаус, які зростають зі збільшенням *x*, для дослідження цих структур необхідні додаткові дослідження ЕПР, такі як: а) кутові ЕПР-дослідження для різних орієнтацій зразків щодо радіочастотного поля і магнітного полів, так, щоб можна було побудувати тензор g; б) з'ясування температурної залежності сигналу ЕПР від кімнатних температур до температури рідкого азоту.

Ключові слова: шаруватий напівпровідник, магнітний сенсор, інтеркаляція, електронно-парамагнітний резонанс (ЕПР).

Annotation. The EPR studies of electrical and magnetic properties of In_4Se_3 intercalated by copper 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. EPR spectra for In_4Se_3 crystal with the impurities of Cu at room temperature are analyzed.

Key words: layered semiconductor, magnetic sensor, intercalation, electron paramagneticrresonance (EPR).

Introduction

Magnetic sensors along with their major constituents such as magnetoresistive structures can be employed 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 utilized as key elements in plenty of security and military systems. Modern sensor types such as AMR (Anisotropic MagnetoResistors), GMR (Giant Magneto-Resistance), SDT (Spin-Dependent Tunelling) and GMI (Giant Magneto-Impedance) sensors are developed to complement the conventional sensors such as fluxgates, induction coils and resonance magnetometers [2]. 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 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]. 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]. 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. 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 throroughly described in [12]. Electron paramagnetic resonance (EPR) or electron spin resonance (ESR) spectroscopy is a method for studying materials with unpaired electrons. The basic concepts of EPR are analogous to those of nuclear magnetic resonance (NMR), but it is electron spins that are excited instead of the spins of atomic nuclei. EPR spectroscopy is particularly useful for studying metal complexes or organic radicals [13]. On the other hand EPR spectroscopy is one of the most powerful methods used for studying the structure and determining the identity of paramagnetic centers or radicals via the *g*–value and the hyperfine coupling (HFCC) coefficient because the nuclei are near the unpaired electron. The HFCC of a given nucleus in a radical is highly sensitive to its chemical environment. Hence, HFCC can be used to determine the spin-density distribution of the radical and also to deduce valuable information about the identity and structure of the radical. However, the *g*-value depends on the spin distribution throughout the radical; thus, it can be significantly affected by intermolecular interactions. Extraction of this information from experimental spectra is not always straightforward, and therefore, quantum-chemical calculations are frequently needed [14].

The purpose of the article

1. To investigate the EPR spectra of $Cu_xIn_4Se_3$ structure in the X-band range as a function of temperature and Cu content x. 2. To determine the g factor of the unpaired electrons in this structure. 3. To investigate the gain or loss of the angular momentum by the unpaired electrons in $Cu_xIn_4Se_3$ structure with the subsequent change in the value of its *g*-factor, causing it to differ from standard g_e.

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 [15]. 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 magnetoactive layers [16]. 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 [17]. 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 [18]. 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 [17, 18]. 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]. To investigate the effect of metallic impurities on the layered In_4Se_3 structure EPR spectra are outlined in the Figures below. EPR spectra have been measured at the Center for Microelectronics and Nanotechnology of the University of Rzeszow. EPR measurements were performed in the X-band on Bruker multifrequency and multiresonance FT-EPR ELEXSYS E580 spectrometer. The temperature of the samples was controlled in the range of 95–300 K using the Bruker liquid N gas flow cryostat with 41131 VT digital controller. Experimental setup in detail is described in [19].

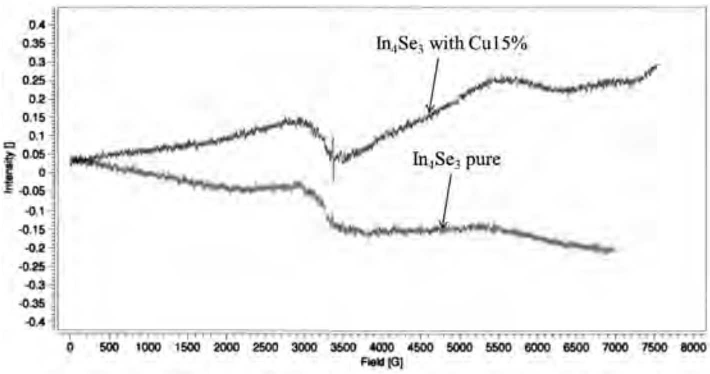

Fig. 1. EPR spectra of In_4Se_3 with Cu 15 % as compared to the pure In_4Se_3

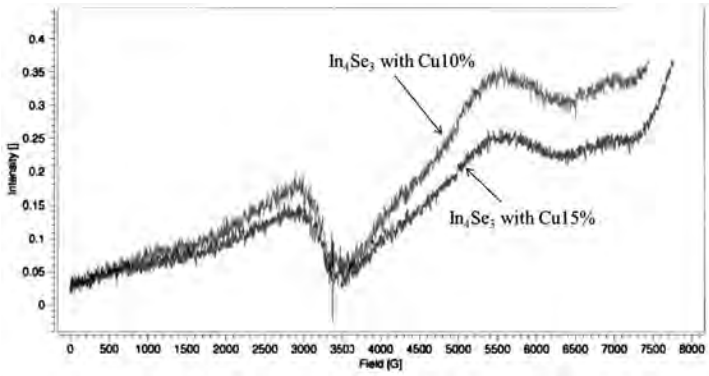

Fig. 2. EPR spectra of In_4Se_3 with Cu 15 % as compared to the pure In_4Se_3 with Cu 10 %

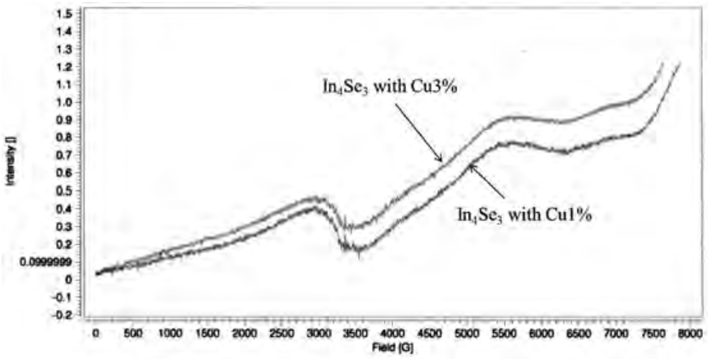

Fig. 3. EPR spectra of In_4Se_3 with Cu 3 % as compared to In_4Se_3 with Cu 1 %

Fig. 1 shows a strong spike for In_4Se_3 (Cu 15 %) for 3400 Gauss region of EPR spectra, in contrast to the pure In_4Se_3.

As it can be seen from Fig. 2 the spike in 3400 Gauss region weakens as copper content decreases.

Fig. 3 shows that even small contents of Cu make the upward trend of the EPR spectra as opposed to the pure In_4Se_3 where the downward trend (see Fig. 1) has been observed. Small spikes at 3400 Gauss are already present at Cu 1 % and Cu 3 % lines.

Conclusions

EPR spectra demonstrate that the presence of Cu makes considerable changes to the EPR spectra of In_4Se_3 structure. This may be due to the traps for charge carriers introduced by the guest Cu which make an impact on the unpaired electrons associated with In or Se atoms. The content of Cu is proved to be a significant factor for affecting the spikes at EPR spectra. g factor of the unpaired electrons was calculated to be 2,017. This value is shown to be within 1 % margin of the standard

g_e = 2,0023 value. Presence of Cu causes an upward trend of the EPR spectra resulting in a signal intensity increase with the rise of the magnetic field. Since the presence of Cu causes a spike in the EPR spectra which grows with the increasing x further EPR studies have to be carried out: *a*) angular EPR studies for various orientations of the samples in respect to RF and magnetic field so that g tensor could be constructed; *b*) temperature dependence of the EPR signal ranging from room conditions down to liquid nitrogen ones.

References

1. Ripka P. Security applications of magnetic sensors. Journal of Physics Conference Series 06/2013; 450(1):2001-. DOI:10.1088/1742-6596/450/1/012001.

2. Ripka P., Janosek M: Advances in Magnetic Field Sensors, IEEE Sens. J. 10 (2010) Issue: 6, 1108–1116.

3. Oyama Y., Tanabe T., Sato F., Kenmochi A., Nishizawa J., T. Sasaki, K. Suto. J. Cryst. Grow. 310, 1923 (2008).

4. 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. No. 7. – P. 80–84 (in ukrainian).

5. Seredyuk B. O. A study of the kinetic properties of nanostructured intercalates of $Ag_xIn_4Se_3$ aimed at the creation of photodetectors / B. O. Seredyuk // millitary-technical book. – 2014. – № 2(11). – P. 52–55.

6. Novoselov K. S., Geim A. K., Morozov S. V., Jiang D., Zhang Y., Dubonos S. V., Grigorieva I. V., Firsov A. A., Science 2004, 306, 666.

7. Garry W. Mudd, Simon A. Svatek Tuning the Bandgap of Exfoliated InSe Nanosheets by Quantum Confinement Adv. Mater. 2013, 25, 5714–5718

8. Ivashchyshyn F. O., Grygorchak I. I., Balaban O. V., Seredyuk B. O. The impact of phase state of guest histidine on properties and practical applications of nanohybrids on InSe and GaSe basis Materials Science-Poland, 35(1), 2017. – P. 239–245.

9. Shvets R. Ya., Grygorchak I. I., Kurepa A. S., Pokladok N. T., Sementsov Yu. I., Dovbeshko G. I., Sheregii Ye., Seredyuk B. Supercapacity of soft-expanded graphite in li-intercalational electric current generation // Acta Physica Polonica A. – 2015. – Vol. 128(2). – P. 208-209.

10. Dalichaouch Y., Czipott, P., Perry A. Magnetic sensors for battlefield applications / Y. Dalichaouch, P. Czipott, A. Perry // Proc. SPIE – 2001. – Vol. 4393. – P. 129–134.

11. Lenz J., Edelstein, A.S. Magnetic Sensors and Their applications. / J. Lenz, A.S. Edelstein // IEEE Sens. J. – 2006. – № 6. – P. 631–649.

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

13. Ira N. Levine (1975). Molecular Spectroscopy. Wiley & Sons, Inc. p. 380.

14. R. Tapramaz˙ E. Türkkan, Ö. Dereli. Experimental and Theoretical Electron Paramagnetic Resonance (EPR) Study on the Temperature-Dependent Structural Changes of Methylsulfanylmethane. Int J Mol Sci. 2011; 12(8): 4909–4922.

15. Nikitin S. A., 2004, Soros. journ.education 8, No. 2, 92.

16. Pokladok N. T., Grygorchak I. I., Lukiyanets B. A., Popovych D. I., Ripetskyy R. I. peculiarites of magnetoresistance in single crystals inse and gase, laser intercalated by chrome оптико-електронні інформаційно-енергетичні технології. 2008. No. 1. – P. 114–118.

17. Stakhira Y. M., Tovstyuk N. K., Fomenko V. L., Grigorchak I. I., Borysyuk A. K., and Seredyuk B. A. Structure, magnetization and low-temperature impedance response of InSe polycrystals intercalated by nickel. Low Temperature Physics. – 2012. – Vol. 38. – No. 1. – P. 69–75.

18. Grygorchak I. I., Vojtovych S A., Stotsko Z. A., Seredyuk B. A., Tovstyuk N. K. Hyper capacity of MCM-41<nematic> supramoleculer structure in the radio-frequency range. Journal of Achievements in Materials and Manufacturing Engineering. – 2011. – Vol. 49(2). – P. 200–203.

19. I. Stefaniuk I. Rogalska P. Potera D. Wróbel. EPR measurements of ceramic cores used in the aircraft industry. NUKLEONIKA 2013;58(3):391−395.