PRESSURE AND STRAIN SENSITIVITY OF InSe AND GaSe LAYERED SEMICONDUCTORS

Z.D. KOVALYUK, M.M. PYRLYA, V.B. BOLEDZYUK, V.V. SHEVCHIK

Institute of Problems of Materials Science, Nat. Acad. of Sci. of Ukraine, Chernivtsi Division
(5, I. Vil'de Str., Chernivtsi 58001, Ukraine; e-mail: `chimsp@ukrpost.ua`*)*

PACS 73.40.-Lq, 71.35.-y, 78.20.-e, 78.66-w

Experimental data on the pressure sensitivity of InSe and GaSe layered semiconductor crystals and their metal intercalates are obtained. From the measurement results, the pressure (dynamic) sensitivity coefficient for these compounds is determined. High values of the pressure sensitivity coefficient for InSe and GaSe crystals and their intercalates at fast-varying pressures ($k_P \approx 10^{-8} \div 10^{-7}$ Pa^{-1}) open a possibility to use them as sensitive elements of overload indicators (accelerometers). Based on the measurements and the calculations carried out for “layered crystal—silicon” structures, it is established that, in the range of relative deformations of the order of 10^{-5} Pa^{-1}, the strain sensitivity factor $k_{\mathrm{T}} = 1300 \div 1500$, while, in the range of relative deformations of 10^{-4} Pa^{-1}, $k_{\mathrm{T}} = 300$. It is found that the strain sensitivity of intercalated layered crystals depends on the degree of overlapping of the atomic orbits of an intercalant and its density.

1. Introduction

With regard for the specific character of the structure of InSe and GaSe layered crystals (van der Waals bonds between layers, strong anisotropy of their properties, peculiarities of the electron and phonon spectra, *etc.*), it was assumed [1–3] that these structures allow one to realize a high pressure sensitivity and, consequently, to create mechanical pressure transducers (pressure measuring devices).

A theoretical prerequisite for the use of layered semiconductors as the sensitive elements (SE) of pressure sensors is the peculiarities of their crystal structure. Under the normal conditions (at the atmospheric pressure), the integral over the interlayer interaction of a layered crystal β has a constant value, while an increase in the pressure results in a change of β due to the overlapping of the wave functions of neighboring layers. The parameter β enters the dispersion law for layered crystals:

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k_{\|}^2}{2m^*}\beta\cos(K_z d), \qquad (1)$$

where $k_{\|}$ denotes the quasimomentum directed along the layer, m^* is the effective mass that characterizes the electron motion in the layer, β is the integral over the interlayer interaction (overlapping), and d is the lattice constant along the hexagonal axis that determines the behavior of charge carriers in the Brillouin zone and, correspondingly, in the whole bulk of the crystal. Therefore, the variation of the dispersion law induces necessarily considerable changes in all kinetic properties of a semiconductor.

As is known [4–6], the intercalation of InSe and GaSe layered semiconductor crystals represents an effective way to control the physical-chemical properties of initial matrices, which opens a possibility to use these compounds not only for fundamental researches but also for solving applied problems, particularly, in the field of sensor engineering.

In technics, static pressures are usually measured with the help of tensoresistive pressure transducers, whose sensitive elements are presented by resistance strain gauges made of a metal (wired or foil) or a semiconductor (nanocrystal or film). The main characteristic that governs the choice of a specific material is the strain sensitivity coefficient k_{T}. Metal resistance strain gauges that were in a wide use earlier are characterized by $k_{\mathrm{T}} \leq 5$, whereas $k_{\mathrm{T}} \approx 50 \div 200$ for silicon elements [4, 5].

This work is aimed at studying the possibility of a practical use of InSe and GaSe layered crystals and their intercalates as the sensitive elements of pressure sensors, accelerometers, and strain gauges.

2. Experimental Technique

InSe and GaSe single-crystal samples used for experimental and test researches were grown by the Bridgman technique. Indium and gallium selenides were intercalated with the help of the electrochemical method in the galvanostatic mode [6–8]. The conductivity anisotropy of the samples used for the electrochemical intercalation reached $10^4 \div 10^6$. The contacts to single crystals were deposited according to the technique described in [9]. The used electrolytes were: 1-N water solutions of LiCl and $BaCl_2$, 0.01-N water solution of lead acetate, and 0.001-N solution of $AlCl_3$ in propylene carbonate. This allowed us to intercalate Li^+, Ba^{2+}, Al^{3+}, and Pb^{2+} ions at the cathodic polarization of a sample. The intercalation of Pb into the matrix of layered semiconductors was performed using the method of combined intercalation [10]. The concentration of the intercalated substance was determined by the amount of charge that had passed through the electrochemical cell, i.e., the controlled parameters in the process of intercalation were the electric current density (j) and the duration of the procedure (t). This process is described by the known relation [11]

$$C_0(i,t) = Ae^{\alpha(t)+\beta(t)}, \qquad (2)$$

where $C_0(i,t)$ is the amount of intercalated ions in a unit volume of the crystal, $\alpha(t)$ and $\beta(t)$ are some linear functions of the intercalation duration, i denotes the current that has passed through the cell, and A is a proportionality factor.

It is worth noting that the necessary condition for the proper investigation of various phenomena in intercalated semiconductors is the identification and the quantitative analysis of an intercalated impurity, which allows one to determine the chemical formula of the final product of the intercalation reaction. In this work, the impurities intercalated into the matrices were identified with the help of the methods of electron-probe X-ray microanalysis (EPMA) for barium and aluminum ions, electron Auger spectroscopy (EAS) for lithium and aluminum ions, and radioisotope analysis for lead ions. The measurements were carried out on a “Superprobe-733” X-ray microanalyzer that enables one to determine the presence of all elements for $z \geq 4$ in a 1-mum-thick layer to within 0.5 at. The Auger spectra of the Li and Al intercalates of InSe and GaSe compounds were studied on a “Jamp-105” scanning Auger microscope that analyzes (qualitatively and quantitatively) the composition of a layer $1 \div 2$ mm in thickness with an energy resolution of $0.5 \div 1.2\%$ at a probe diameter of $5 \div 500$ mum.

The pressure sensitivities of InSe, GaSe, and their intercalates were investigated in a special high-pressure cell, where the necessary pressure (up to 150 kg/cm^2) was reached by the admission of a compressed gas (N_2, Ar, CO_2) into the inner volume. In order to study the dynamics of electric properties under the action of pressure, the cell body had electric outputs and inlet and bleed needle valves, which allowed us to study the pressure sensitivity of the layered compounds in the admission and bleed modes. The researches were performed on samples $5 \times 2 \times 0.5$ mm^3 in size, whose orientation relative to the crystallographic axis is shown in Fig. 1.

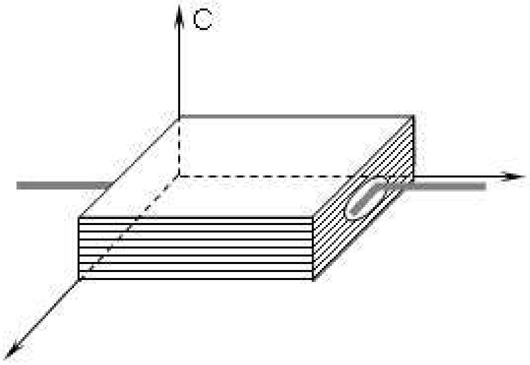

Fig. 1. Orientation of a layered crystal relative to the crystallographic axes when measuring the pressure sensitivity

The electric contacts were deposited both on the ends of the samples and on their opposite base planes. To avoid the long-term relaxation, the samples were heated in darkness to 100 °C during 24 h.

We have investigated the tensoresistive effect in A^3B^6 layered semiconductors and their intercalates. Crystal silicon served as an elastic element (cantilever). Elastic elements made of crystalline materials (particularly, silicon) are characterized by nearly ideal elastic properties [7] and significantly smaller errors of the hysteresis and the linearity as compared with metal ones. The layered semiconductor was fixed on the silicon surface with the help of a K-300 glue.

3. Results and Their Discussion

According to the experimental results, the prevailing effect in layered semiconductors is the so-called dynamic sensitivity effect. In other words, the static (“bulk”) effect of the baric sensitivity is small as compared with the sensitivity to a fast-varying pressure, overload, or shock wave. The typical form of the pressure-induced excitation process in a layered crystal is depicted in Fig. 2. The time dependence of the shock perturbation $Uc(t)$ in InSe and GaSe crystals was investigated on a special shock stand with the use of a storage oscilloscope S8-13 and a strain amplifier “Topaz-4”. The pulse duration was the same for all the samples and amounted to t_1=1 ms. Table 1 presents the experimental values of the time dependences of the pressure excitation $Uc(t)$ of InSe, GaSe, and their intercalates. As follows from the obtained data, the characteristics of the pressure excitation process for the intercalated crystals increase by 1-1.5% as compared to the initial InSe and GaSe samples. It is also worth noting that the parameters τ and

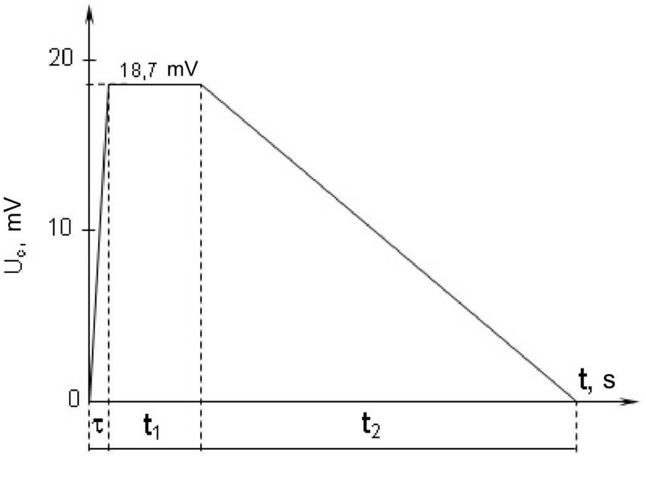

Fig. 2. Time dependence of the pressure-induced excitation in a layered crystal. U_c is the amplitude of the signal under the action of an external pressure, τ is the pulse rise time, t_1 is the pulse duration, and t_2 is the pulse drop time. The numerical values of the parameters are given in Table 1

t_2 for $Pb_{0.03}Li_{0.5}InSe$, $Pb_{0.03}Li_{0.5}GaSe$, $Al_{0.4}InSe$, and $Al_{0.4}GaSe$ intercalates are practically equal to the corresponding parameters of the initial InSe and GaSe samples. It is established that the form of the dependence of the signal amplitude $Uc(t)$ presented in Fig. 2 does not depend on both the configuration of contacts and the form of a semiconductor or an intercalate under study.

The measurement data allow us to determine the coefficient of pressure dynamic sensitivity for "pure" and intercalated InSe and GaSe (Table 2).

According to [12, 13], the specificity of a structure of layered crystals results in the fact that the uniform pressure applied to a layered crystal is equivalent, to a high accuracy, to the one-sided pressure along the **c** axis. A certain advantage consists also in the independence of the dynamic pressure sensitivity of the configuration of electric contacts. That is why a conclusion can be made that the revealed dynamic sensitivity effect is inappropriate for measurements of a static or slowly varying pressure. This effect can be used to register fast-varying pressures, overloads, and shock waves.

Table 1. Characteristics of the time dependence of the pressure excitation for layered crystals and their intercalates

Sensitive element	Pulse rise time τ, ms	Pulse drop time t_2
InSe	5.20	3 min 40 s
GaSe	4.75	2 min 55 s
$Li_{0.5}InSe$	5.26	3 min 43 s
$Li_{0.5}GaSe$	4.81	2 min 58 s
$Ba_{0.4}InSe$	5.28	3 min 47 s
$Ba_{0.4}GaSe$	4.83	3 min 02 s

High values of the pressure sensitivity coefficient of InSe and GaSe single crystals for fast varying pressures have opened a possibility to use them as overload indicators (accelerometers) based on the functional dynamic baric dependence of the electrokinetic properties of layered semiconductors. It follows from the studies performed that the most suitable material for the fabrication of the sensitive elements of accelerometers is indium monoselenide crystals characterized by a high sensitivity ($k_P \cong 10^{-8} \div 10^{-7}$ Pa^{-1}) and a comparatively low specific resistance (the resistance of elements was equal to $\sim 10^2 \div 10^4$ Ohm).

Investigations of the cyclicity of the effect of an increase in the baric sensitivity for fast varying pressures with the use of InSe, GaSe, and their intercalates as sensitive elements have demonstrated that this phenomenon is reproducible for 20–25 cycles. By measuring the time dependences of the baric excitation in InSe, GaSe, and their intercalates (Table 1), we have established the absence of a residual value of the signal $Uc(t)$ after the pulse drop within the measurement error (0.3–0.5%). Tests of the model of a mechanical part and a secondary accelerometer transducer in the range of overloads 30–70 g testify to the linearity of the output signal in the acceleration range under study.

The measurements performed for the "layered semiconductor–silicon" structures demonstrate that, in the region of relative deformations of the order of 10^{-5} Pa^{-1}, the strain sensitivity coefficient $k_\mathrm{T} = 1300 \div 1500$, whereas, at relative deformations of the order of 10^{-4} Pa^{-1}, $k_\mathrm{T} \approx 300$. A high value of the strain sensitivity coefficient of InSe and GaSe semiconductors is related to the specific nature of the tensoresistive effect in these

Table 2. Pressure sensitivity coefficient for layered crystals and their intercalates

Sensitive element	Pressure coefficient k_P, $\times 10^{-8}$ Pa^{-1}
InSe	2.44
GaSe	1.14
$Li_{0.5}InSe$	2.67
$Li_{0.5}GaSe$	1.45
$Pb_{0.03}Li_{0.5}InSe$	2.38
$Pb_{0.03}Li_{0.5}GaSe$	1.27
$Ba_{0.4}InSe$	2.64
$Ba_{0.4}GaSe$	1.85
$Al_{0.4}InSe$	2.47
$Al_{0.4}GaSe$	1.29

crystals. In addition to the common tensoresistive effect, a deformation of layered semiconductors results in the effect of the overlapping of the wave functions of neighboring microlayers, which results in a high strain sensitivity of elements produced from InSe and GaSe crystals at relative deformations of 10^{-5} Pa^{-1}. At higher relative deformations, the strain sensitivity of layered crystals is mainly determined by the common tensoresistive effect, whose strain sensitivity coefficient (k_{T}) is higher than that in isotropic or weakly anisotropic semiconductors (Si, Ge, *etc.*) due to a specific structure of InSe and GaSe. The both tensoresistive effects in layered semiconductors are stationary and reproducible.

An effective way to increase the strain sensitivity coefficient of InSe and GaSe layered crystals in the region of relative deformations up to 10^{-5} Pa^{-1} is the intercalation method [2, 14]. Layers of the basic substance in an intercalated semiconductor alternate with impurity layers. Such a structure determines a considerable variation of the interlayer interaction integral [13] and thus allows one to change β choosing the sort and the concentration of an intercalated impurity. It is worth noting that the impurity atoms do not occupy definite positions in intercalated impurity compounds and "rotate" along a circle, whose radius ρ is inversely proportional to the atomic weight of the impurity m ($\rho \sim 1/m$, "Jahn–Teller pseudoeffect") [14]. At high impurity concentrations, the "orbits" of intercalated atoms can overlap due to mechanical stresses. The degree of overlapping of the orbits of impurity atoms and their concentration determine the strain sensitivity of intercalates of layered crystals.

We have investigated the tensoresistive effect on InSe films grown on substrates of oxidized silicon (the elastic element was a silicon cantilever). The strain sensitivity coefficient $k_{\mathrm{T}} \approx 300 \div 500$ (at relative deformations below 10^{-4} Pa^{-1}) is practically equal to the values of k_{T} in InSe single crystal samples.

4. Conclusions

We have studied the pressure sensitivity of InSe and GaSe layered semiconductors and their metal intercalates. It is established that the dynamic sensitivity effect is dominant in layered crystals, whereas the static (bulk) effect is small as compared with the sensitivity to fast-varying pressures. High values of the pressure sensitivity coefficient of InSe and GaSe single crystals and their intercalates ($k_P \approx 10^{-8} \div 10^{-7}$ Pa^{-1}) for fast-varying pressures open possibilities for their use as the sensitive elements of overload indicators.

The phenomenon of tensoresistive effect is investigated in the A^3B^6 layered semiconductor ("pure" or intercalated one) – elastic element (crystalline silicon) structures. The strain sensitivity coefficient k_{T} for the described structures (the case of a central force) is calculated. The measurements and calculations performed for "layered semiconductor–silicon" structures have established that, at relative deformations of the order of $\sim 10^{-5}$ Pa^{-1}, the strain sensitivity coefficient $k_{\mathrm{T}} = 1300 \div 1500$, whereas $k_{\mathrm{T}} = 300$ at relative deformations of $\sim 10^{-4}$ Pa^{-1}.

1. B.A. Luk'yanets, K.K. Danilevich-Tovstyuk, and K.D. Tovstyuk, Fiz. Tverd. Tela **23**, 2998 (1981).
2. K.D. Tovstyuk, *Semiconductor Materials Science* (Naukova Dumka, Kiev, 1984) (in Russian).
3. L.M. Zaichenko, A.I. Seredyuk, V.D. Fotii, and Yu.R. Shevchuk, Tekhnol. Konstr. Elektr. App., No. 2, 57 (2004).
4. E.S. Levshina and P.V. Novitskii, *Electric Measurements of Physical Quantities* (Energoatomizdat, Leningrad, 1989) (in Russian).
5. *Semiconductor Strain Gauges*, edited by M. Din (Energiya, Moscow, 1965) (in Russian).
6. V.B. Boledzyuk, Z.D. Kovalyuk, and M.M. Pyrlya, Neorg. Mater. **45**, 1303 (2009).
7. Z.D. Kovalyuk, M.M. Pyrlya, and V.B. Boledzyuk, Nauk. Visn. Chern. Univ. Fiz. Elektr. Issue 6, 31 (1999).
8. S.S. Ishchenko, M.T. Ivaniichuk, D.V. Korbutyak *et al.*, Fiz. Tekhn. Polupr. **15**, 2045 (1981).
9. L.A. Demchina, Z.D. Kovalyuk, and I.V. Mintyanskii, Prib. Tekhn. Exper. **2**, 219 (1980).
10. Z.D. Kovalyuk, M.M. Pyrlya, A.I. Seredyuk, and K.D. Tovstyuk, Neorg. Mater. **29**, 1652 (1985).
11. I.I. Grigorchak, Z.D. Kovalyuk, and S.P. Yurtsenyuk, Izv. Akad. Nauk USSR. Ser. Neorg. Mater. **17**, 412 (1981).
12. N.A. Abdulaev, Fiz. Tverd. Tela **48**, 623 (2006).
13. G.A. Belen'kii. E.Yu. Salaev, and R.A. Suleimanov, Usp. Fiz. Nauk **155**, 89 (1988).
14. B.A. Lukiyanets, K.D. Tovstyuk, V.V. Boichuk, and K.K. Danilevich-Tovstyuk, Phys. Stat. Sol. (b) **124**, 693 (1984).

Received 28.12.10.
Translated from Ukrainian by H.G. Kalyuzhna

БАРИЧНА ТА ТЕНЗОЧУТЛИВІСТЬ ШАРУВАТИХ НАПІВПРОВІДНИКІВ InSe та GaSe

З.Д. Ковалюк, М.М. Пирля, В.Б. Боледзюк, В.В. Шевчик

Резюме

Одержано експериментальні результати по дослідженню баричної чутливості шаруватих напівпровідникових кристалів InSe, GaSe та їх металевих інтеркалятів. Результати вимірювань дозволили визначити коефіцієнт баричної (динамічної) чутливості для даних сполук. Високі значення коефіцієнта баричної чутливості монокристалів InSe, GaSe та їх інтеркалятів ($k_P \approx 10^{-8}$–10^{-7} Па$^{-1}$) для швидкозмінних тисків відкрили можливість для їх використання у ролі чутливих елементів індикаторів перевантажень (акселерометрів). З проведених вимірювань та розрахунків для структур шаруватий напівпровідник–кремній встановлено, що в області відносних деформацій $\sim 10^{-5}$ Па $^{-1}$ коефіцієнт тензочутливості $k_{\rm T}$ = 1300–1500, в області відносних деформацій $\sim 10^{-4}$ Па$^{-1}$ значення $k_{\rm T} = 300$. Визначено, що тензочутливість інтеркалятів шаруватих кристалів залежить від ступеня перекриття орбіт атомів інтеркальованої домішки та її концентрації.