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Layered crystals $FeIn_2Se_4$, In_4Se_3 and heterojunctions on their basis

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A new heterojunction (GP) p-$FeIn_2Se_4$–n-In_4Se_3 was formed by the mechanical contact of the $FeIn_2Se_4$ plate with the van der Waals surface of In_4Se_3. Investigation of Volt-Farada's, spectral characteristics and temperature dependences of the VAC of the heterojunction. On the basis of the analysis of electric and photovoltaic characteristics of the GP, a high-quality zone diagram was constructed.The region of spectral photosensitivity of p-$FeIn_2Se_4$–n-In_4Se_3 GP which is in the range 0.7-1.3 eV, is established..

Keywords: layered crystals, heterojunction, spectral characteristics.

Методом механического контакта пластины $FeIn_2Se_4$ с ван-дер-ваальсовой поверхностью In_4Se_3 сформирован новый гетеропереход (ГП) p-$FeIn_2Se_4$–n-In_4Se_3. Исследованы вольт-фарадные, спектральные характеристики и температурные зависимости ВАХ гетероперехода. На основе анализа электрических и фотоэлектрических характеристик ГП построена его качественная зонная диаграмма. Установлена область спектральной фоточувствительности ГП p-$FeIn_2Se_4$–n-In_4Se_3, которая находится в пределах 0,7 – 1,3 эВ.

Шаруваті кристали $FeIn_2Se_4$, In_4Se_3 і гетеропереходи на їх основі. В.М.Катеринчук, З.Д.Ковалюк, Б.В.Кушнір, В.В.Нетяга, І.Г.Ткачук

Методом механічного контакту пластини $FeIn_2Se_4$ з ван-дер-ваальсовою поверхнею In_4Se_3 сформовано новий гетероперехід (ГП) p-$FeIn_2Se_4$–n-In_4Se_3. Досліджено вольт-фарадні, спектральні характеристики і температурні залежності ВАХ гетеропереходу. На основі аналізу електричних і фотоелектричних характеристик ГП побудована його якісна зонна діаграма. Встановлено область спектральної фоточутливості ГП p-$FeIn_2Se_4$-n-In_4Se_3, яка знаходиться в межах 0,7 – 1,3 еВ.

1. Introduction

In recent years, $A^{II}B_2^{III}X_4^{VI}$ semiconductors (II is Fe, Mn, Ni, or Co; III is Ga or In; and VI is S, Se, or Te) containing elements with unfilled d-shells have been intensively investigates. Layered crystals $FeIn_2Se_4$ were obtaining and investigated, for example, in [1-5], and the crystals In_4Se_3 in [6-7]. However, these materials are still remains understudied in fundamental and practical terms.

$FeIn_2Se_4$ and In_4Se_3 layered crystals, which can be both n- or p-type of conductivity, are advanced materials to create a photosensitive heterostructures based on them [8-10]. These materials with different symmetry and lattice periods allow the method of van der Waals contact of their surfaces to create quality heterojunctions [11].

The aim of this study was to preparing and studying of electrical and photoelectric characteristics of the p-$FeIn_2Se_4$–n-In_4Se_3 heterojunctions for the first time.

2. Experimental

The In_4Se_3 single crystals were grown by the Czochralski method and characterized by a pronounced layered structure over the whole length of a sample. The mirror-like cleaved surfaces (not requiring additional treatment) of the obtained crystals without scratches and other damages were suitable to create a heterojunction by van der Waals contact. Based on the Hall effect, it is established that In_4Se_3 samples had the n-type conduction with concentration of the majority charge carriers $n = 2{\cdot}10^{15}$ cm^{-3} and mobility perpendicular to C $\mu_n = 20$ cm^2/($V{\cdot}s$), where C is the crystallographic axis which coincides with the normal to the layer plane.

As the wide band-gap frontal semiconductor were used crystals of $FeIn_2Se_4$ that were grown by the Bridgman technique. Based on the Hall effect was found that the samples had the p-type conduction. At room temperature for the $FeIn_2Se_4$ crystals the concentration of the majority charge carriers and the Hall mobility along layers were measured to be $p = (2 \ldots 3)\ 10^{16}$ cm^{-3} and $\mu_p = 10$ cm^2/$V{\cdot}s$, respectively.

The heterojunctions p-$FeIn_2Se_4$ - n-In_4Se_3 were prepared by the method of mechanical contact of $FeIn_2Se_4$ plate with the Van-der-Waals surface of In_4Se_3. Pure indium was used for current contacts. To eliminate the non-ohmicity of the back contact p-$FeIn_2Se_4$/In, was used a method consists of formation of a large number of recombination centers in the region of the semiconductor which is adjacent to the heterointerface "semiconductor/metal" by means of damaging the $FeIn_2Se_4$ mechanically [12].

The structure and lattice parameters of the crystals were established from X-ray diffraction measurements in CuKα radiation by means of a DRON-2.0 installation assembled according to the Bragg-Bertano scheme. The obtained X-ray diffraction patterns were processed by using the LATTIK-KARTA software.

The current-voltage (I-V) and capacitance-voltage (C-V) characteristics of the HJ were studied on a SOLARTRON SI 1286, SI 1255 setup interfaced with a computer. All the measurements were carried out at room temperature. Temperature dependences of the current-voltage characteristics were also investigated with the purpose to establish the current flow mechanism through the HJs.

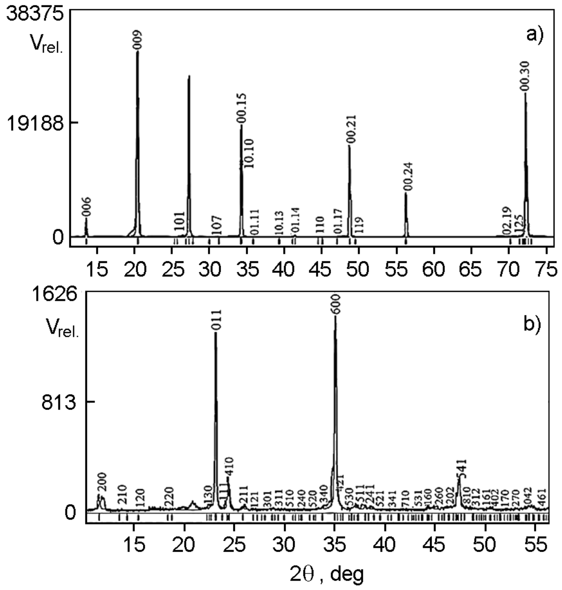

Fig. 1. XRD patterns of the $FeIn_2Se_4$ (a) and In_4Se_3 (b) layered compounds.

The sensitivity spectral areas were identified by MDR-3 monochromator with a resolution of 2.6 nm/mm at room temperature. All spectra were normalized relative to the number of incident photons.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $FeIn_2Se_4$ (a) and In_4Se_3 (b) layered compounds. An X-ray spectrum analysis has shown that the $FeIn_2Se_4$ crystals have a hexagonal structure with the lattice parameters a=4.0492 Å and c=39.0231 Å. These data agree well with those reported by Reil and Haeuseler [13]. An X-ray diffraction pattern of the $FeIn_2Se_4$ (a) registered from a cleaved surface demonstrates the 00l reflections (l = 6, 9, 12, 18, 21, 24, 30, 33). The absence of additional peaks is evidence that the composition of the grown $FeIn_2Se_4$ crystals corresponds to its formula.

The XRD analysis revealed that the structure of the In_4Se_3 substrate had the following lattice constants: a=15.3435 Å, b=12.4080 Å, c=4.0442 Å in the orthorhombic space group P_{nnm} and are in agreement with the published values [14].

The capacitance-voltage characteristics of p-$FeIn_2Se_4$-n-In_4Se_3 heterojunctions in C^{-2} vs. U coordinates at room temperature and different frequencies are shown in Fig. 2. The Linear C^{-2}-U dependences correspond to the abrupt type of p-n-junction [15]. The

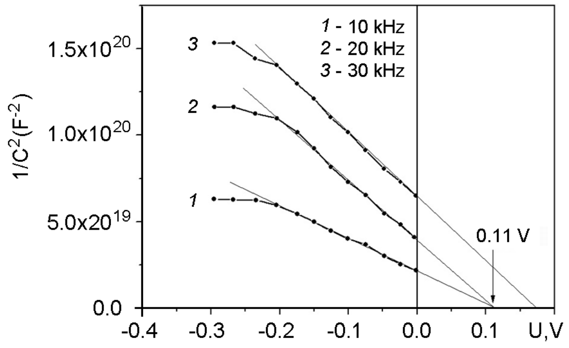

Fig. 2. Capacitance-voltage characteristics of p-$FeIn_2Se_4$ - n-In_4Se_3 heterojunction at different frequencies.

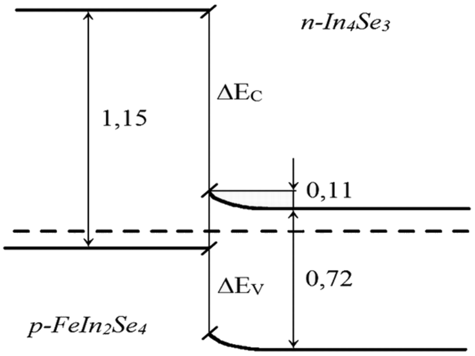

Fig. 3. Energy band diagram of the heterojunctions p-$FeIn_2Se_4$–n-In_4Se_3. All values are expressed in eV.

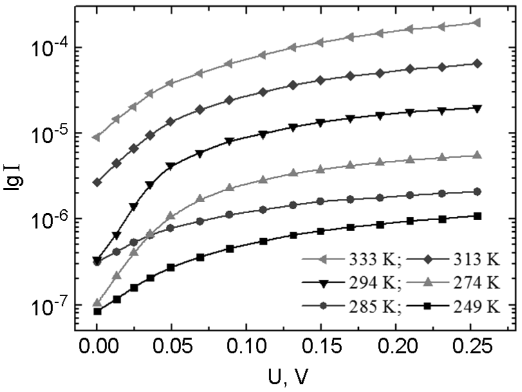

Fig. 4. The I-V characteristics of the p-$FeIn_2Se_4$–n-In_4Se_3 heterojunctions measured at different temperatures T under forward bias in the semilogarithmic scale.

C-V curves at reverse bias have two slopes that corresponds to two main ionization mechanisms of impurities: generating one type of carriers at low bias voltages and two types – at high reverse voltages [16].

The disagreements in frequency dependence are more difference in the high-frequency region of test signal. Therefore, to correctly determine the value of potential barrier ϕ_b is necessary to choose a cut-off continuation of the linear dependence of C-V characteristic received at frequencies $\omega \to 0$ [8]. Fig. 2 shows that the capacitive cut-off biases at frequencies of 10 and 20 kHz respond to the value ~ 0.11 V.

The energy band diagram of the heterojunction constructed using potential barrier ϕ_b is shown in Fig. 3. The band gap values were taken from [13, 14]. The positions of the Fermi level in the n-In_4Se_3 and p-$FeIn_2Se_4$ were estimated from the majority carrier concentrations by the formula:

$$\left|E_{C(V)} - E_F\right| = kT\ln[N_{C(V)}/N_{n(p)}],$$

where $E_{C(V)}$ – the conduction band bottom (valence band top), E_F – the Fermi energy, $N_{C(V)}$ – the effective density of states in the respective band, $N_{n(p)}$ – the concentration of majority carriers.

It is shown that, the breaks of ΔE_C and ΔE_V allowed bands stimulate unidirectional injection of holes from p-$FeIn_2Se_4$ in n-In_4Se_3 under forward bias.

Fig. 4 shows the current-voltage characteristics of the heterojunction p-$FeIn_2Se_4$ - n-In_4Se_3 measured at different temperatures under forward bias in the semilogarithmic scale. The relatively low value of potential barrier does not reveal the true mechanism of current transport through the p-n-junction. Although the current-voltage dependence has exponentially character, the slope of the current-voltage characteristics in voltage range of 0 – 0.1 V are different at various temperatures: the lower the temperature - the smaller the slope of the current-voltage characteristics. This behavior of I-V curves indicates that the potential barrier increases with decreasing temperature and the shunt currents, on the contrary, reduced.

However, the true diffuse currents under forward bias still not large enough to prevail shunt currents through the p-n-junction. The p-n-junction fully opened with direct voltage increasing and the all voltage drop falls on the bulk part of heterojunction. Fig. 4 shows that, the I-V characteristics at different temperatures are shifted parallel, indicating the features of current transport in the neutral parts of the heterojunction.

The photosensitivity spectra of the p-$FeIn_2Se_4$–n-In_4Se_3 heterojunction are shown in Fig. 5. It is well seen that the

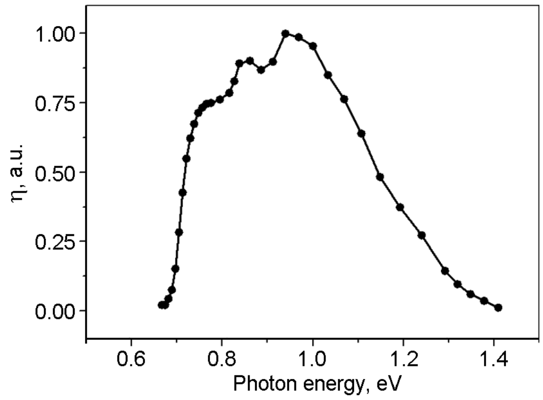

Fig. 5. The photosensitivity spectra of the p-$FeIn_2Se_4$–n-In_4Se_3 heterojunction measured at room temperature.

photosensitivity spectrum is limited from both sides and corresponds to light absorption in narrow band gap In_4Se_3 (E_g ~ 0,72 eV at 300 K) and wide band gap $FeIn_2Se_4$ (E_g ~ 1,15 eV at 300 K) which is characteristic of the spectrum shape for heterojunctions.

4. Conclusions

A new heterojunction based on layered crystals p-$FeIn_2Se_4$ and n-In_4Se_3 were prepared by mechanical van der Waals contact. The measured electric characteristics (I-V, C-V and photosensitivity spectra) testify to satisfactory quality of the obtained heterojunctions. The spectral sensitivity of p-$FeIn_2Se_4$–n-In_4Se_3 heterojunctions was identified and had the value 0.7 – 1.3 eV. The current transport mechanisms were analyzed by investigating temperature dependences of the I-V characteristics. The energy band diagram of the p-$FeIn_2Se_4$–n-In_4Se_3 structure is constructed. It revealed that, the dominating current transport mechanisms through the p-$FeIn_2Se_4$–n-In_4Se_3 interface caused by a hole diffusion due to the asymmetrical gaps.

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