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Excitonic photoconductivity of heterostructures based on gallium and indium selenides

V.M.Katerynchuk, Z.D.Kovalyuk, I.G.Tkachuk

Chernivtsi Department, I.Frantsevich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine,
5 Iryna Vilde Str., 58001 Chernivtsi, Ukraine

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Present spectra of photosensitivity of various types of heterojunctions based on layered crystals $A^{III}B^{VI}$ made of the Van der Waals connection of pairs on heteromer as well as covalent. We also discuss the features of excitonic bands of the crystals. Examples of the first type, the heterojunction are pairs of *n*–InSe–*p*–InSe and *p*–GaSe–*n*–InSe and *p*–GaSe–*n*–In_4Se_3, *n*–SnS_2–*p*–InSe. As examples of heterojunction with a the covalent bond are the other systems: In_2O_3–InSe, In_2O_3–Ga_2O_3–GaSe, In_2O_3–Ga_2O_3–GaTe. These heterojunctions formed with participation of their oxides of different chemical nature. In the case when the oxide has leading properties, it plays a direct active role in the heterojunction formation. However, the formation of the heterojunction using high temperature heating of the substrates at air, naturally leads to uncontrolled growth of its own oxides on *p*–GaSe and *p*–GaTe which shows dielectric properties.

Keywords: gallium selenium, indium selenium, layered crystal, heterostructure.

Представлены спектры фоточувствительности различных типов гетеропереходов на основе слоистых кристаллов $A^{III}B^{VI}$, изготовленных как с ван-дер-ваальсовой связью пар на гетерогранице, так и с ковалентной, обсуждаются особенности их екситонних полос. Примерами первого типа гетероперехода послужили пары *n*–InSe–*p*–InSe, *p*–GaSe–*n*–InSe, *p*–GaSe–*n*–In_4Se_3, *n*–SnS_2–*p*–InSe. В качестве гетероперехода с ковалентной связью оказались другие системы: In_2O_3–InSe, In_2O_3–Ga_2O_3–GaSe, In_2O_3–Ga_2O_3–GaTe. В случае, где оксид обладает ведущими свойствами, он играл непосредственную активную роль в формировании гетероперехода. Вместе с тем, формирование гетероперехода с помощью высокотемпературного нагрева подложек на воздухе непринужденно приводило к неконтролируемому росту собственных оксидов на *p*–GaSe и *p*–GaTe, которые проявили диэлектрические свойства.

Екситонна фотопровідність гетероструктур на основі селену галію і селену індію. *В.М.Катеренчук, З.Д.Ковалюк, І.Г.Ткачук*.

Представлено спектри фоточутливості різних типів гетеропереходів на основі шаруватих кристалів $A^{III}B^{VI}$, виготовлених як з ван-дер-ваальсівським зв'язком пар на гетеромежі, так і з ковалентним, обговорюються особливості їх екситонних смуг. Прикладами першого типу гетеропереходу є пари *n*–InSe–*p*–InSe, *p*–GaSe–*n*–InSe, *p*–GaSe–*n*–In_4Se_3, *n*–SnS_2–*p*–InSe. В якості гетеропереходу з ковалентним зв'язком виявилися інші системи: In_2O_3–InSe, In_2O_3–Ga_2O_3–GaSe, In_2O_3–Ga_2O_3–GaTe. У випадку, де оксид володіє провідними властивостями, він відігравав безпосередню активну роль у формуванні гетеропереходу. Водночас, формування гетеропереходу з допомогою високотемпературного нагріву підкладок на повітрі, невимушено приводило до неконтрольованого росту власних оксидів на *p*–GaSe і *p*–GaTe, які проявили діелектричні властивості.

1. Introduction

Interface of heterostructures is a transition range from one crystal lattice to another one. The translation symmetry in this range is broken and atom vibrations can differ from those in the bulk of the crystals. Usually the binding energy of excitons is smaller in comparison to the room temperature thermal energy kT and, therefore, they can be observed in absorption spectra only at the low temperatures. As light absorption in heterostructures takes place on the interface, where phononvibrations differ from that in bulk, it is worth to expect changes in excitonic spectra. The interface range with changed phonon energies can exceed the lattice parameters of both contacting phases.

In this paper we present photosensitivity spectra for various heterostructures based on layered III–VI compounds and peculiarities of their excitonic bands discussed.

2. Experimental

There are many reasons to use layered crystals InSe, GaSe, GaTe and others for preparation of heterostructures. Firstly, these compounds have a layered crystalline structure. It makes it possible to receive substrates with (001) plane without dangling bonds due to the presence of weak Van der Waals forces between the layered. The absence of dangling bonds determines a low density of electron surface states. As a result, the method of Van der Waals contact between two heterogeneous materials is widely used in the technology of production of heterostructures based on the layered crystal [1]. In this paper this method was used to prepare *n*–InSe–*p*–InSe, GaSe–InSe, In_4Se_3–GaSe, and InSe–SnS_2 heterostructures. Secondly, low density of the surface electron states can be achived in an oxide-semiconductor system, as it occurs in modern silicon technology. It is caused by displacement of the interface into the depth of silicon. Oxidation of the layered crystal also leads to formation on their surfaces of indium and gallium oxides, which can play functional role in operating the heterostructures. At the same time, oxidation is a simple way to create potential barriers [2]. By using this method the In_2O_3–InSe heterostructures were prepared. In order to prepare heterostructures, containing In_2O_3(Sn), we have used the method of pyrolysis of chemical solutions of indium and tin chlorides [3]. By using this method the In_2O_3–Ga_2O_3–GaSe, and In_2O_3–Ga_2O_3–GaTe heterostructures were obtained. The presence

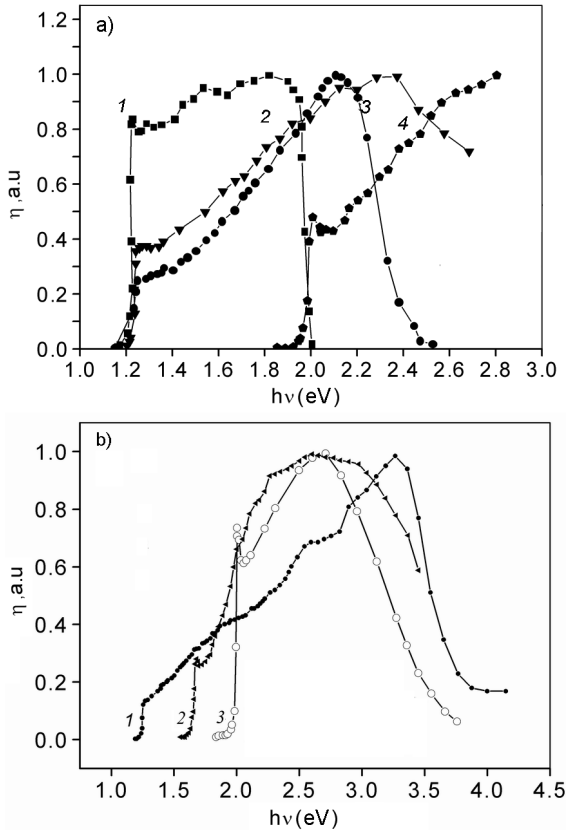

Fig. 1. Spectra of relative quantum efficiency of photocurrent of various heterojunctions at room temperature. *a) 1* — GaSe–InSe; *2* — *n*–InSe–*p*–InSe; *3* — SnS_2–InSe; *4* — In_4Se_3–GaSe. *b) 1* — In_2O_3–InSe; *2* — In_2O_3–Ga_2O_3–GaTe; *3* — In_2O_3–Ga_2O_3–GaSe.

of intrinsic oxide Ga_2O_3 for GaSe and GaTe is a result of substrates heating in the air at formation of In_2O_3(Sn) films.

Photosensitivity spectra for the different heterostructures were investigated at the room temperature in photodiode mode by means of installation with a MDR-3 monochromator. Its spectral resolution was below 26 Å/mm.

3. Results and discussion

All the obtained spectra were divided on two groups. For comparison the heterostructures with weak Van der Waals coupling at the interfaces were included to the first group. The heterostructures with strong covalent bonding, which appers at oxide-semiconductor interfaces during oxide growth at the crystal substrates, belong to the second group.

Photosensitivity spectra of the heterostructures are shown in Fig. 1.

As one can see from the presented spectra, there is a slight peak of different intensity depending on heterostructures type at their long-wavelength edge. It appearance

Table. Parameters of crystal lattices and excitons in the layered materials and lattice mismatches in the heterostructures

Material	γ–InSe	β–GaTe	ε–GaSe	SnS_2	In_4Se_3	In_2O_3	Ga_2O_3
a, (Å)	4.002	17.404	3.755	3.648	15.296	10.11	10.00
b, (Å)	–	4.077	–	–	12.308	–	–
c, (Å)	24.946	10.456	15.95	5.899	4.0806	–	–
R_0(meV)	14.5	18.9	20	–	–	–	–
r_B(Å)	50	31.1	41.5	–	–	–	–
lattice mismatches, δ_a(%)							
	n–InSe–*p*–InSe	SnS_2–InSe	GaSe–InSe	In_4Se_3GaSe	In_2O_3–InSe	Ga_2O_3–GaTe	Ga_2O_3–GaSe
	0	9.25	6.37	121.16	86.56	54.04	90.80

was supposed to be due to formation of excitons. Comparison of these spectra to the long-wavelength edge of the room temperature absorption spectra for the crystals of InSe [4, 5] GaTe [6] and GaSe [7, 8] shows that analogous excitonic peaks are not observed. It is related to the fact that the exciton binding energy in the layered materials prevails under the room temperature thermal energy kT. Some exciton parameters and the lattice parameters of the crystals are listed in Table 1: a, b, and c are the lattice parameters; R_0 is the Rydberg constant; r_B is the Bohr radius of excitons.

As one can see from Table, for all the heterogeneous structures we have $\delta_a > 1$ %. However the peculiarities of formation of the heterostructures based on the layered crystals make it possible to receive their high parameters in spite of essential values of δ_a. It is worth to note that there is a correlation between the lattice mismatch and the intensity of the excitonic bands in the photosensitivity spectra. The higher is δ_a the clearer excitonic peak becomes (Fig. 1a — curves *1* and *4*; Fig. 1b curves *2* and *3*). Such regularity makes it possible to have found a serial dependence of the excitonic bands as early as at liquid nitrogen temperature. The analogous dependence in the absorption spectra of the crystal was observed only at the liquid helium temperature [5, 6, 8, 9]. Therefore investigations of the excitonic photosensitivity have advantages over those for absorption spectra. At the same time the nature of the chemical bonding at the interface does not affect essentially the excitonic bands. For the both heterostructure groups there are the excitonic peaks of photosensitive spectra and their intensity depends on heterostructure kind and parameter *elta*. The appearance of the excitonic bands in the room temperature photosensitivity spectra on contrary to their absence in the absorption spectra can be explained by a change of phonon vibrations at the interface regions where light is absorbed. Such a change is caused by lattice mismatches destroying the translation symmetry at the interfaces.

4. Conclusions

Quantum efficiency spectra of photocurrent were investigated for heterostructures based on layered crystals of InSe, GaSe, GaTe, In_4Se_3, and SnS_2. The structures under investigations were divided by two groups with respect to chemical bonding nature at the interfaces — Van der Waals type or covalent. The photosensitivity spectra of the both type heterostructures showed different intensity peaks located at the long-wavelength edge attributed to the formation of excitons. The appearance of excitonic photosensitivity is supposed to be due to change of phonon vibrations at the interfaces because of the lattice mismatches.

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