THE OPTIC AND PHOTOELECTRIC PROPERTIES OF POLYTYPES OF MONOCLINIC $TlInS_2$

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The crystals of polytypes of monoclinic modification $TlInS_2$ with parameters of elementary cell c≈15Å, c≈60Å и c≈120Å have been obtained. The optic and photoelectric properties of obtained samples near the edge of their fundamental absorption have been studied; the positions of edge excitons in given polytypes have been defined. The aging process of obtained polytypes has been studied.

The five crystal modifications of $TlInS_2$ compound are known nowadays. The two of them (monoclinic and threeclinic) have layered structure, and two (tetragonal and orthorhombic) have layered-chain structure. The crystals of fifth modification are related to hexagonal crystal structure [5, 6]. Moreover, the $TlInS_2$ of monoclinic structure has some polytypic varieties. The parameter c of crystal lattice of these polytypes practically changes multiply from c≈15Å till c≈240Å [7].

The coincidence of interesting semiconductor properties along with presence of monoclinic modification of phase transformations in $TlInS_2$ crystals increases the interest to their investigation. It is revealed, that the monoclinic $TlInS_2$ endures the ferroelectric phase transition at temperature decrease at T_c~200K, to which the phase transition in disproportional phase precedes at T_i~216K [8]. As a rule, the due attention to real crystal structure wasn't paid at investigation of physic properties of these crystals, including dielectric ones. Besides, in papers [9, 10] was shown, that these properties significantly change from sample to sample on example of investigation of dielectric properties of $TlInS_2$ monocrystals. The last one is caused by the fact, that investigated samples often present themselves the polytype mix.

The samples, consisting different polytypes of $TlInS_2$ of monoclinic modifications, were specially chosen among crystals from different technological groups in paper [9]. Moreover, according to roentgenograms, the only polytype with parameter c≈15Å existed in pure form, the insignificant presence of other polytypes took place in samples with c≈60Å and c≈120Å.

In the given paper the investigation results of optic and photoelectric properties of "pure" polytypes of monoclinic modifications $TlInS_2$ with parameter of elementary cell, which is equal to ~15Å, 60Å or120Å near the edge of their fundamental absorption. The aging process of obtained polytypes has been studied.

The polytypes of monoclinic $TlInS_2$ with parameters of elementary cell, which are equal to c=15.082Å (β=99,62°); c=59,87Å (β=96,0°) and c=119,31Å(β=99,0°) (later c≈15Å, c≈60Å and c≈120Å) had been obtained by the method, described in paper [11]. For this purpose, the prepared monocrystal samples, splitted of one ingot, grown up by the method of directed crystallization with use of stoichiometric melt in vacuum 10^{-6} millimeter of mercury were treated by thermal treatment according to modes, given in paper [11]. The polytypic homogeneity, quality and crystal-graphical parameters of obtained crystals were controlled by the taking off the crystallograms from planes *00l* in angle limit 5-70^0. The values of β angles were defined from weisenbergograms.

The spectral dependencies of optical properties of obtained samples near edge of their fundamental absorption with permission not worse than 10^{-3} meV were investigated on installation, constructed on base of DFS-24 spectrophotometer. The FEU-79 was used in capacity of receiver. The spectral dependences of absorption coefficient α were calculated on the base of transmission spectrums of two plane-parallel plates of one and the same polytype of different thickness (10÷30 mcm) [12], splitted off on the basal plane of one monocrystal ingot consecutively. Moreover, the difference of reflection coefficients R of different samples of one and the same semiconductor, taking place in layered crystals [13]. For this case the formula for absorption coefficient α, which is analogical one to paper [12], can be easily obtained:

$$\alpha = \frac{1}{d_2 - d_1} \ln \frac{I_1}{I_2} \frac{(1-R_2)}{(1-R_1)}, \qquad (1)$$

where $d_1, d_2 (d_2 > d_1)$ are sample widths, I_1,I_2 are intensities of radiation, passed through the samples, and R_1, R_2 are values of. The values of reflection coefficients at different wave lengths were calculated on the base of the values of refraction coefficients, defined from interference figure, clearly registered even at significant widths (~1mm). The use of formula (2.1) was excused by the fact, that in some samples of one and the same polytype R_1 and R_2 differed till 1.5 times. The photoconductivity spectrums (PC) were taken off with the help of MDR-23 monochromator at synchronous detection of PC signal, the intensity of flux of light was modulated with frequency 83 Hz. All investigations were carried out in nonpolarized light at room temperature at normal light incidence on layer surfaces, the contacts were situated on the surfaces, perpendicular to the layers.

The spectral dependences of absorption coefficient $\alpha(h\nu)$ of samples of different polytypes of monoclinic crystal $TlInS_2$ at 300K are given on the fig.1.

The strong growth of α and maximum appearance, the energy position of which differs in different polytypes, is the character peculiarity of spectrums of optical absorption coefficients of investigated crystals. As a whole, the

absorption spectrum of crystal, investigated by us, are similar with ones, observed by other authors earlier in $TlInS_2$ crystals and their peculiarities are caused by the formation near the edge of fundamental absorption of direct free excitons [14]. For polytype with the energy position of exciton is E_{ex}=2.454eV, for polytype with c≈60Å the energy position of exciton is E_{ex}=2.388eV, for polytype with c≈120Å the energy position of exciton is E_{ex}=2.425 eV. The difference in E_{ex} position had been revealed earlier only in paper [14] for two samples $TlInS_2$, related to monoclinic crystal structure, however, the crystal-graphical parameters of investigated crystals weren't be given.

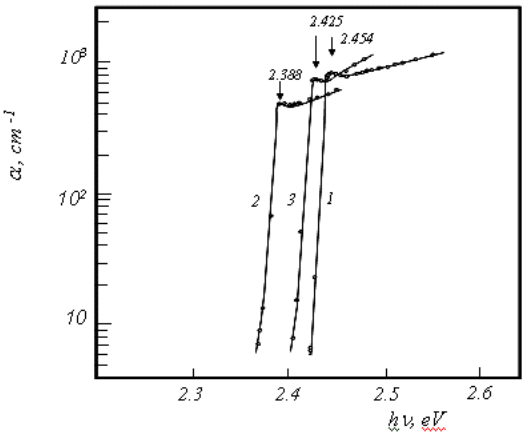

Fig.1. The dependence of absorption coefficient (α) on photon energy of polytype samples: 1- c≈15Å, 2- c≈60Å, 3- c≈120Å (300K).

The non-monotone character of E_{ex} change with increase of crystal lattice "c" parameter attracts attention. The calculations of band structure of $TlInS_2$ crystals are absent in references. The difficultness in definition of atom coordinates in samples, presenting the polytype mixture is the one of the reasons of above mentioned. The analysis of crystal-graphical parameters of polytypes of monoclinic $TlInS_2$, as having in references, so obtained in given paper, allows to conclude, that volumes of elementary packs, from which the polytypes have been created (pack width ~15 Å), just differ in different polytypes. Consequently, the elementary packs are deformed differently in crystals of different polytypes.

Let's estimate the value of forbidden band width E_g in different polytypes, caused by this deformation, in frameworks of model of deformation potential in approximation of quasi-tetragonal crystal ($D_a = D_b = D_{//} \neq D_{\perp} \approx D_c$, where D_a, D_b and D_c are values of deformation potentials of crystal along axes a, b and c, correspondingly). Supposing, that ionization energy of excitons of all polytypes are similar and shift of their energy position is caused by only E_g (ΔE_g) shift in the result of deformation one can write[15]:

$$\Delta E_g = D_{//}(U_a + U_b) + D_{\perp}U_c, \qquad (2)$$

where $D_{//} \approx -7.3эВ$, $D_{\perp} \approx 11.9эВ$ for monoclinic $TlInS_2$ [14], and U_a, U_b and U_c are equal to relative deformation$\Delta a/a$, $\Delta b/b$ and $\Delta c/c$, correspondingly. Taking the polytype c≈15Å with E_{ex}=2.454 eV for the base, on known parameters a, b and c, one can estimate E_g shift in other polytypes in respect of polytype with c≈15Å. Using the values of crystal-graphical parameters, defined by us, for polytypes c=15,083Å (a=10,98Å, b=10,906Å), and c=59,87Å (a≈10,96Å, b≈10,97Å [16] from (3.1), we obtain ΔE_g ≈-120 MeV, whereas its value in experiment is ~ -65 MeV. As it is seen, the usable model in given case correctly describes the E_g change in different polytypes. The only E_g shift, caused by deformation along axis c of crystal $D_{\perp}U_c \approx$ -30 MeV can be estimated for polytype with c=119,309Å because of the data absence about parameters of elementary cell a and b. The estimations show, that the total change of parameters of elementary cell a and b ($\Delta a+\Delta b$) of polytype with c=119,31Å relatively polytype with c=15,083Å should be ~ 0,08Å for ideal agreement with experiment.

The energy decrease of exciton absorption in set of polytypes with c=15Å, 120Å, 60Å is accompanied by the decrease of its absorption coefficient. The last one can be caused by the competition of nearest minimums of conduction band in crystals of $TlGaSe_2$ type and by hit of discrete levels of direct exciton in region of continuous spectrum of additional minimum with deformation increase. The observable value decrease of maximum of exciton absorption can be connected with broadening of exciton peak in the result of heterogeneous deformation of multipack polytypes, relatively polytype with c=15Å.

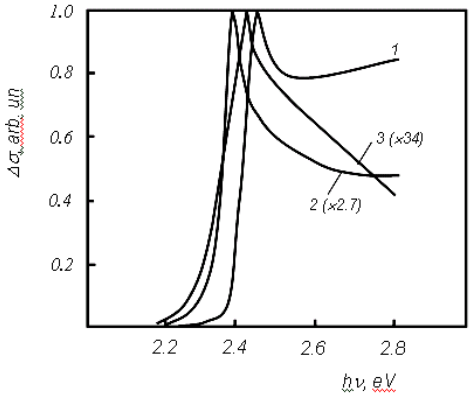

Fig.2. The conduction dependencies ($\Delta\sigma$) on photon energy of polytypes: 1- c≈15Å, 2- c≈60Å, 3- c≈120Å (300K).

The spectral distribution of conduction change ($\Delta\sigma$) of polytype samples $TlInS_2$ at their radiation by monochromatic light is given on the fig.2. It is need to note, that investigations were carried out on decade sample of each type and curves, given on the fig.2, are characteristics for polytypes of monoclinic modification $TlInS_2$, studied by us. The conduction curves were normalized on equal quantum density and on voltage unit, applied to the sample:

$$\Delta\sigma = \frac{\Delta U}{R_L n(h\nu) S U}, \qquad (3)$$

where ΔU is value of photoconductivity signal; R_L is loading resistance ($R_L << R_0$ is sample resistance); $n(h\nu)$ is number of incident quantum in time unit on sample square unit at given monochromator crack; S is sample square; U is voltage, applied to the sample. The curves 1-3 relate to spectrums of PC samples of polytypes $TlInS_2$ with $c \approx 15$Å, $c \approx 60$Å and $c \approx 120$Å, correspondingly. The maximums of all curves are given to unit for the comparison comfort of spectral dependences. As it is seen from the fig.2, the practice coincidence of maximums of absorption and PC spectrums take place. The polytype with $c \approx 15$Å has the more short-wave maximum (2.454 eV), and polytype with $c \approx 60$Å has the more long-wave one (2.388 eV) of PC. The positions of exciton peak as in Ph spectrum, so in absorption spectrum are close and are situated in 2.425-2.430 eV limits for polytype with $c \approx 120$Å.

The practice coincidence of maximums of Ph and absorption spectrums of each polytype, probably, is caused by the small ionization energy of edge excitons ε_i (15-20 MeV)$<kT$, which are thermionized at $T \approx 300$K after photoexcitation. It is note that photosensitivities of separate polytypes significantly differ. So the polytype with parameter of elementary cell $c \approx 15$Å has the most photosensitivity, polytype with $c \approx 120$Å has the less photosensitivity (fig.2). As all samples have been obtained by thermal treatment of similar duration from one crystal ingot, so the only treatment temperature is the main their difference. Let's note, that growth of this temperature is accompanied by PC decrease as in energy region of direct exciton, so in energy region $h\nu > E_g$. Moreover, PC increase in region of long-wave spectrum wing $h\nu < E_{ex}$ is observed. In paper [17] it is shown, that presence of sulfur vacancies, with concentration increase of which PC in $h\nu \geq E_g$ region decreases is character defect for layered $TlInS_2$. It is possible to suppose, that sulfur vacancies, the concentrations of which increase with increase of treatment temperature, form in obtaining process of polytypes of monoclinic $TlInS_2$ by the way of high-temperature treatment. That's why it is clear, that PC of polytypes, obtained by us, should be decreased with increase of their treatment temperatures [11] that takes place in our case.

It is need to note, that along with above mentioned investigations, the process investigations of time stability of obtained crystal polytypes $TlInS_2$ of monoclinic modification were also carried out. These investigations were carried out during several years both on crystals, being polytype mixture, and on separate polytypes. It had been established, that the crystals of homogeneous polytypes are few stable in the difference from crystals, being polytype mixture. Approximately in several months, the reflex appearance, relating to other polytypes, was observed in crystals, presenting themselves the polytypes with parameters $c \approx 15$Å and $c \approx 120$Å on diffractograms, taken off the surface [001]. The polytype with parameter value $c \approx 60$Å is more stable in the comparison with them. So for example, the appearance of lines, peculiar to polytype with parameter of elementary cell $c \approx 15$Å is revealed in diffractograms of polytype samples with parameter value of elementary cell $c \approx 60$Å after six months. The reflex appearance of polytypes with values of parameter of elementary cell $c \approx 15$Å and $c \approx 60$Å, besides the main ones was observed on diffractograms of polytype samples with value of parameter of elementary cell $c \approx 120$Å after four months. These changes were accompanied by significant intensity decrease and broadening of reflexes with indexes *00l*, that proves on our opinion, about disorder of layer attachment in crystals, carrying out in time. The influence of the flux of light and multiple processes of strong polytype sample cooling-heating in temperature interval 300-77K are the main external factors, accelerating aging process. The samples, presenting initially polytype mixture, are stable and their physical properties are unchangeable during several years. The described above aging processes find their reflection in physic, in particular, optical and photoelectric properties of these crystals and are the subject of individual publication.

Conclusions

1. The positions of edge excitons in polytype samples of monoclinic $TlInS_2$ with parameters of elementary cell $c \approx 15{,}082$Å, $c \approx 59{,}87$Å and $c \approx 119{,}31$Å which are equal to 2.454 eV, 2.388 eV and 2.425 eV correspondingly, are defined by investigations of their fundamental absorption edge. The well agreement of given energies with photoconductivity maximums of given crystals has been revealed.

2. The aging processes of obtained samples have been studied by method of roentgen diffraction. It is shown, that samples of "pure" polytypes are unstable and the appearance of other polytypes is observed in them with time. The factors, accelerating aging process have been revealed.

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MONOKLİN $TlInS_2$ POLİTİPLƏRİNİN OPTİK VƏ FOTOELEKTRİK XASSƏLƏRİ

Elementar qəfəsin c≈15Å, c≈60Å və c≈120Å parametrləri ilə monoklin modifikasiyalı $TlInS_2$ kristalları alınmışdır. Optik və fotoelektrik tədqiqat nəticəsində alınmış politiplərdə eksitonların yerləri müəyyən edilmişdir. Politiplərdə "köhnəlmə" prosesləri müşahidə edilib tədqiq edilmişdir.

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ОПТИЧЕСКИЕ И ФОТОЭЛЕКТРИЧЕСКИЕ СВОЙСТВА ПОЛИТИПОВ МОНОКЛИННОГО $TlInS_2$

Получены кристаллы политипов моноклинной модификации $TlInS_2$ с параметрами элементарной ячейки c≈15Å, c≈60Å и c≈120Å. Изучены оптические и фотоэлектрические свойства полученных образцов вблизи края их фундаментального поглощения, определены положения краевых экситонов в указанных политипах. Исследованы процессы старения полученных политипов.

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