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PRODUCTION OF $Ge_{1-x}Ln_xS$ MONOCRYSTALS AND THEIR ELECTROPHYSICAL AND PHOTOELETRIC PROPERTIES

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ABSTRACT

Among semiconductor materials wich can be citilized for recording optical information and holograms of considerable interest are layered materials.Inparticulas, GeSmonocrystals belong to them. A unique device of germanium sulphide that can contain a great quantity of lithium ionehaz been created recently of the University North Carolina. Such material is perfectly suitable as starting stock in manufacturing solar panels. Along with these properties germaniummonosulphideposseffes change-over and memory effects. To widen the scope of using GeSmonocrystal it was introduced into the matrix of atoms of rare-earth elements (Nd,Sm,Gd). The present research explores the formation of $Ge_{1-x}Ln_xS$ (where Ln-Nd.Sm,Gd) monocrystals and studies their electrophysical and photoelectrical properties.

Keywords

Layered crystals; semiconductor materials; monocrystals; photoelectrical propesties

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INTRODUCTION

Ample potentialities of using layered semiconductors in modern electronics caused considerable interests in them.

A number of layered crystals, including GeS possess high diffraction efficiency, utmost resolution, a possibility of repeated re-recording of information. Theses crystals do not require special chemical treatment after exposure, they have rather great thickness. Their physical properties are markedly influenced by imparities of rare-earth elements(in particular, Nd, Sm and Gd).

SYNTHESIS AND PRODUCTION OF MONOCRYSTALS

For synthesizing Ge_{1-x} Ln_xSpolycrystals (with, ln-Nd, Sm, Gd; x=0,005; 0,01) the method of direct fusion of calculated amounts of germanium, sulphur and rare-earth elements was used. As materials for synthesis of the polycristals were employed germanium with specific resistance of 50 ohm.cm, brand “B5” sulphur, brand “Нм-2”neodym, brand “См-2” samarium and brand “Гм-1” gadolinium.The calculated stoichiometricweighed amounts of germanium, sulphur and rare-earth elements were loaded into a quartz ampoule of 15-20 cm in length and 1,8÷22 cm in diameter. The ampoule was pumped out down to pressure equal to 10^{-3} mm of mercury column and then sealed off. To prevent explosion of the ampoule the amount of the substance was limited to 10-15 g. it should be said that for providing full safety germanium was pulverized. Owing to this method we have managed to synthesize Ge_{1-x} Ln_xS polycrystals.

The synthesizing process was performed in two stages. At first the ampoules were being heated to 300°C in afurnace with the rate of 3-5 deg./min. and allowed to stand for 10-12 hours. Afterwords temperature was being raised with the rate of 2-3 deg./min. to complete melting of germanium and maintained for 18-20 hours. Bridgeman’s method was used for growing the $Ge_{1-x}Ln_x$ S monocrystals. The temperature in the upper part of the furnace was by 50°C more while in the lower part of the furnace it was by 50°C less than the melting point of the appropriate substance. The velocity of the ampoule in the furnace was 2-3 mm/hour which was quite favourable for the formation of monocrystals of the obtained samples.

After the above mentioned synthesizing process a comprehensive research was carried out comprising differential thermal analysis (DTA) and X-ray phase and lysis (RPA) [2].

Through the use of DTA thermal effects were determined-phase transitions and melting point. The rate of heating and cooling was in the range from 6 to 9 deg./min. As distinct from $Ge_{1-x}Ln_xS$ polycrystals, thermal effect was observed on a GeSthermogram at 590°C. An effect conforming to polymorphous transformation of germanium monosulphide shows itself well in heating curves after annealing. This effect is less evident in cooling curves. By analogy with sulphide and selenide it is supposed that the effect observed at 590°C conforms to transformation of the second type [3].

The authors of paper [4] explored the region of the Ge-S system constitution diagram close to 50 percent of S with the use of DTA method. It has been shown that the effect at 590°C previously detected by phase transition of GeS in solid state is due to unbalanced crystal lization alloys and disappears after prolonged(about 300 hours) annealing of samples. In contrast with germanium monosulphide in $Ge_{1-x}Ln_x$Ssolid solutions, no type of thermal effect of 590°C is observed.

When a GeS crystal is doped with impurities of rare-earth elements (REE) (Nd, Sm, Gd) a number of additional effects are brought about which are related to the formation of defects because of deviation of a composition from stoichiometric one. In case of a significant difference in sizes of an atom of an impurity being introduced (REE) and a replacing atom (Ge) the process of doping is accompanied by the emergence of additional intrinsic point defects and the change in from of their location in the crystals. The presence of a large number of vacancies as well as extended flat defects and screw dislocations is responsible for the appearance of stresses in crystal lattice. Some lattice disorder caused because of this will influence shifts in GeS crystal melting point (Table 1).

Table 1. Shifts in GeS crystal melting point

Alloy composition	Melting point, °C
GeS	655
$Ge_{0,995}Nd_{0,005}S$	622
$Ge_{0,995}Sm_{0,005}S$	637
$Ge_{0,995}Gd_{0,005}S$	626
$Ge_{0,99}N_{0,01}S$	607
$Ge_{0,99}Sm_{0,01}S$	630
$Ge_{0,99}Gd_{0,01}S$	610

X-ray phase analysis (RPA) is the most versatile and acceptable method among methods a sample was of physic-chemical analysis. To perform RPA a sample was pulverized diffractograms were taken on D8 ADVANCE

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diffractometer under copper irradiation. Diffraction recordings were conducted in a 10°≤20°≤ 80° angle range at room temperature. Interplanar distances have been computed according to TOPAS and EVA program. Radiographic studies have demonstrated that doping with REE does not alter structure and lattice parameters practically remain the same as in nondoped matter.

However, a change in height and width of diffractogram peaks was found to be marked. With a rise in doping degree the peaks lower and spread. The witnessed transformation of X-ray diffractograms is indicative of deformations caused by impurities and of the occurrence of matrix lattice stressed state.

Low solubility and considerable deviation of REE impurity distribution from statistical one in semiconductors is a typical phenomenon [5] and is explained by REE tendency to form intricate complexes and associates the formation of which leads to the creation of stresses in crystal lattice and this is in line with results of analysis of X-ray diffractograms.

ELECTRO-PHYSICAL PROPERTIES OF $Ge_{1-x}Ln_xS$ MONOCRYSTALS

The peculiarities of electro-physical properties of complex crystals are most easily revealed in the course of studying transfer phenomena in them. Volt-ampere characteristics (VAC) and temperature dependences of electric conduction and mobility allow to determine mechanisms of transfer and scattering of charge carriers.

Temperature dependences of electric conduction of $Ge_{1-x}Ln_xS$ crystals within a temperature range from 200 to 800K were studied. The results of this study are demonstrated in Fig.1. as follows from Fig.1, in a temperature interval from 200 to 500 K conduction increases exponentially with a rise in temperature. This is due to increase in concentration of charge carriers as mobility depends little on temperature which does not practically tell on the course of change in conduction.

With further rise temperature there occurs depletion of impurities, concentration remains constant and dependence of electric conduction of $Ge_{1-x}Ln_xS$ crystals reveals that these crystals are typical impurity semiconductors.

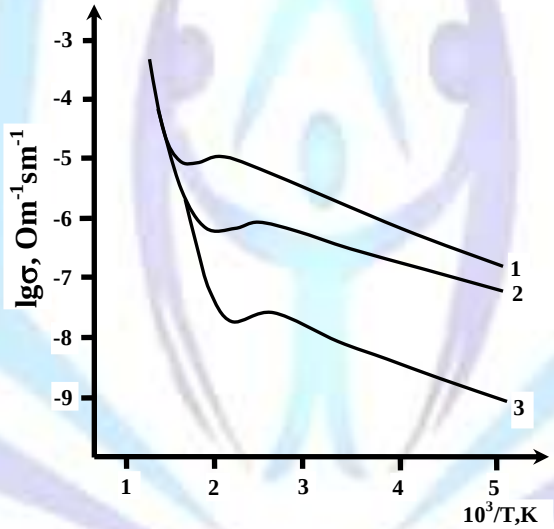

Fig 1: Temperature dependence of Ge_{1-x} Ln_x S (Ln-Nd; Sm; Gd; x=0,005; 0,01) monocrystals.

As follows from Fig.1, electric conduction within a temperature range from 200 to 400 K goes up with increase in temperature at the expense of growth in the number of carriers from impurity levels in the conduction area. With addition of impurities from REE atoms a change in electric conduction in $Ge_{1-x}Ln_xS$ develops in the same way, i.e. at low temperatures relatively small increase in electric conduction is detected, a drop in electric conduction with increase in temperature region of depletion area which resembles the behavior of resistance in metals. Here the number of charge carriers remains constant while mobility is limited mainly by lattice scattering, thus, mobility and electric conduction diminish.

With increasing temperature thermal excitation of carriers will begin manifesting itself through forbidden gap. As the number of thermally excited carriers grows with increasing temperature nearly exponentially, transition region of impurity and intrinsic conduction turns out to be extremely narrow. Intrinsic carriers quickly become predominant and conduction grows exponentially with increase in temperature. As follows from Fig.1, with increasing content of impurities temperature corresponding to the start of intrinsic conduction shifts towards lower temperatures. The width ofGeS crystal forbidden gap determined from high-temperature slope of lgσ relationship (l/T) was found to be equal to 1,63 eV and impurity activation energy was 0,68eV [6].

The number of researches dedicated to studying threshold change-over in amorphous and crystalline semiconductors has considerably grown recently. There were studied static volt-ampere characteristics (VAC) of Ge_{1-}

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$_xLn_xS$ monocrystals at 300 K. The monocrystals looked like flat parallel plates up to 8×10×0,2 mm in size. When studying VAC of $Ge_{1-x}Ln_xS$ monocrystals Ag served as contacts. The results of the study are given in Fig.2.

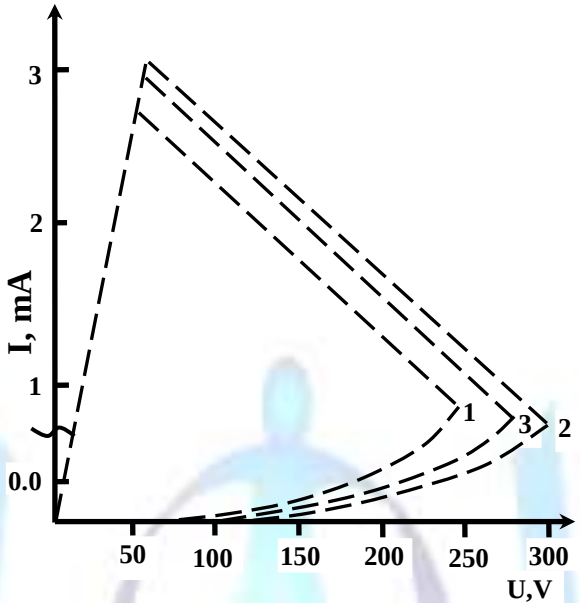

Fig 2: VAC of monocrystals. 1-GeS; 2-$Ge_{0.995}Nd_{0.005}S$; 3-$Ge_{0.99}Nd_{0.01}S$ at T=300K

As follows from Fig.2,at low values of voltage the dependence of strength of current on voltage proves to be linear and the contact is ohmic. However, with increasing voltage to a certain value the samples transit step wisely from high-ohmic state to low-ohmic one.

For all studied crystals were observed symmetrical VAC with a sharply marked portion of negative differential resistance. It indicates that the studied crystals possess change-over properties with memory. The amount ofNdimpurity affects the threshold value of voltage at which the change overoccurs. Similar results were obtained with Sm and Gd impurities.

There exist two mechanism for explaining the change-over effect: electronic and thermal. Usually the change-over effect or thin films is chiefly explained by electronic mechanism and on plenar samples it is explained by thermal mechanism. The change-over effect in the investigated materials develops in the following way: during voltage feed the heating of material in a conduction cord takes place which results in disintegration of its partially ordered structure and transition to amorphous state. When voltage is removed and rapid cooling occurs the materials does not have time to crystallize again and a device goes from the state with high conduction to the state with low conduction. On slow cooling the material can crystallize again.

Thus, depending on a device design and change-over conditions it is possible to obtain VAC both “with memory” and “without memory” on the same material.

Many physical properties of semiconductors are determined by nature, state and positioning of local levels in their forbidden gap. The study of volt-ampere characteristics (VAC) allows to judge about such important parameters of trapping sites as depth of occurence, concentration and section of trapping and else provides information on nature of distribution of local levels in forbidden gap of high-ohmic materials. [8]

A Volt-ampere characteristic of monopolarinjection current plotted to double logarithmic scale usually comprises three portions.

As follows from Fig3, the first of these portions obeys Ohm’s law, the second one ($J\text{-}U^2$) corresponds to current limited by bulkcharge and the third portion corresponds to a rapid increase in current at the voltage which is known as ultimate trap filling voltage.

At low values of voltage injection of carriers from electrode is negligibly small and current obeys ohm’s law.When traps are absent current is limited by space charge. At this voltage the concentration of free carriers injected from electrode begins to prevail appreciably over thermally balanced concentration of carriers.

After this point VAC for flat electrodes obeys square law: $J\text{-}U^2$. So, when there are no traps, current is proportional to a square of applied voltage. In case when there are only shallow. Traps, only some part of carriers being injected from electrode are found to be free. The rest of the carriers are captured by traps. In case of the presence of shallow. Traps VAC of a high-ohmic solid body obeys square law as well.

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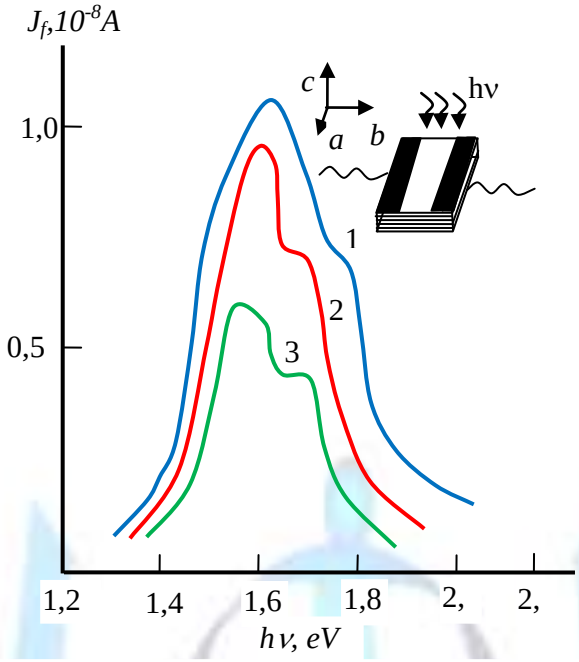

Fig 3: Injection currents of monocrystales 1.GeS; 2 $Ge_{0.995}$ $Nd_{0.005}S$; 3.$Ge_{0.99}$ Nd $_{0.01}$ S

Unordered systems contain deep traps too. In case when shallow and deep traps are homogeneously distributed inside the forbidden gap. VAC will be steeper [9].

Thus, analysis of VAC of layered GeS and $Ge_{1-x}Ln_xS$ (Ln-Nd, Sm, Gd; x =0.005 and 0.01) monocrystals shows that the mechanism of current passage is governed by monopolar injection.

PHOTOELECTRIC PROPERTIES OF MONOCRYSTALS

A number of unique devices made from germanium monisulphide have been created in the last years. As GeS absorbs solar energy very well, this is the property which is supposed to allow production of sufficiently effective solar batteries on its base [10]. That is why the study of physical properties including photoelectric properties of GeS and $Ge_{1-x}Ln_xS$ is of both practical and scientific interest.

Certain progress in the experimental study of energy structure of layered crystals has been achieved through the use of various spectroscopic research methods. Valuable data on the structure of energy spectrum of electrons in crystals can be obtained from spectral distribution of photoconduction.

The results of a research on spectral distribution ofGeS and $Ge_{1-x}Ln_xS$ photoconduction at constant electric field applied along layers, were determined over a wide temperature range between 80 and 320K. When measuring photoconduction spectra in non-polorized light two maxima appear simultaneously (Fig4). The studies of photoconduction spectra in polarized light point to the presence of two absorption edges corresponding to polarization of E||a and E||b.

Impurity atoms of REE (Nd, Sm) form an additional maximum (Fig5) at temperature above 200K. At room temperature (T=300K) two maxima are observed in GeSmonocrystal photoconduction spectra: one (when photon energy is hv=1.65 eV) manifests itself in polarization the other (when photon energy is hv=1.73 eV) in E||b polarization.

With decreasing temperature both intrinsic maxima shift to the short-wave region with the rate of:

Respectively. Moreover, with a drop in temperature the second maximum is sharply marked which is explained by growth in anisothropy of complex monocrystals.

Unlike spectral distribution of GeSmonocrystal photoconduction additional maximum shows itself in photoconduction spectrum of $Ge_{1-x}La_xS$ triple compound (x=0.005) at photon energy of -1.2ev and the said maximum is related to defect formation because of deviation from stoichiometricequilibrium.A significant difference in atomic radii of Nd impurity being introduced and Ge atom being replaced leads to the generation of additional point defects in doping process. Nd element impurities replacing cations and not having one electron less than Ge atoms in the outer shell produce an accepter effects. So, Nd atoms dissolve in vacancies, i.e process of cation injection filling takes place.

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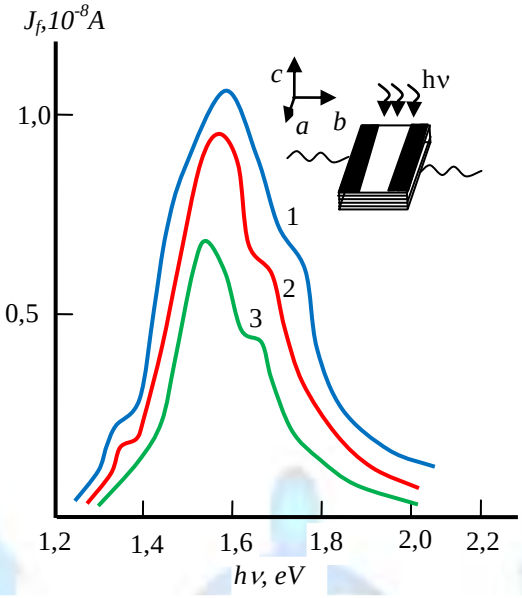

Fig 4: Spectral distribution of GeS crystal photoconduction 1-300K; 2-200K; 3-80k

Owing to this, the concentration of holes falls abruptly resulting in a sharp drop in speedy electric conduction and an increase in intergral photoconduction. When Nd atoms are localized in vacancies, the concentration of point defects of new type-namely, impurity replacement defects responsible for impurity photoconduction with a maximum at hv=1.2 eV grows higher. An intricate electronic configuration of REE atoms permits to carry out these phenomena at a temperature above 200K.

Defect formation in germanium monosulphide causes lattice disordering which manifests in a decrease in intensity and suppression of photoconduction intrinsic maxima . [11]

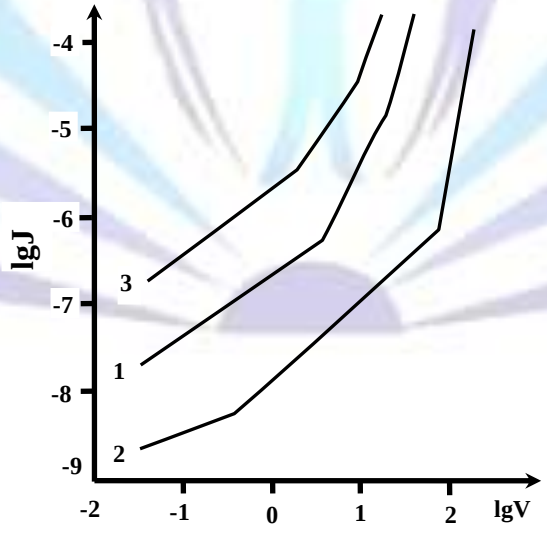

Fig 5: Spectral distribution of $Ge_{1-x}La_xS$ crystal photoconduction (x=0.005)

CONCLUSION

A layered semiconductor-germanium monosulphide- is a promising material for energetics. With the aim of broadening possibilities of using this crystal various methods exerting influence, are employed. It is shown that doping of GeS crystals with rare-earth element impurities is an effective means of controlling their photoelectric properties. The result of studies performed in the research have allowed to raise photoconduction of layered GeS crystals as well as to exert influence on nature of photoconduction polarizing spectrum.

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Author' biography with Photo

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June 5, 1960, was born in Guba, Azerbaijan.

In 1977 he graduated from high school number 36 in Baku

He is married and has 2 children

In 1992 he defended his thesis on "The electro-optical properties of single crystals Ge1-xLnxS (Ln-Nd; Sm; HD).

Field of study: GES layered crystal structures of nano-based high-power capacity and efficiency of processes.

Semiconductors: heterotransition, based on a layered crystal GES.