THE PHOTOELECTRIC PECULIARITIES OF ELECTROGRAPHIC LAYERS OF TRIGONAL SELENIUM, CHEMICALLY PURED AND DOPED BY SODIUM

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The electrograpic layers on the base of trigonal selenium, chemically pured and doped by sodium, in binding material are prepared. The main parameters and characteristics of the layers with sodium impurity and without it are investigated. It is shown that sodium impurity especially improves the layer properties.

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INTRODUCTION

The electrography, the principles of which are connected with achievements of semiconductor physics, is the one of the most distributed and intensively developed reproduction methods. The wide application of electrography causes the necessity in improvement of present photoreceptors and formation of new ones. The photosensitivity in visual and especially red regions of spectrum is the important criterion. Nowadays, the schemes of xerographic image reproduction based on the use of amorphous selenium, A^2B^6 type compounds, organic semiconductors and etc, are realized. The investigations on formation of photoreceptors on the base of amorphous silicon enriched by oxygen are carried out.

The elementary semiconductor Se notices attention of investigators by its unique properties. It has the high photosensitivity, it can be obtained in amorphous, (glassy), and crystal (trigonal and monoclinic) states. All these properties make it irreplaceable one at formation of different transformers (first power rectifiers, photoreceptors, vidicons, photoisolators and etc). The high technological effectiveness of selenium (low melting point, possibility of marking on the surface of any form and etc) is the important. The wide use of Se in different technique fields constantly stimulates the investigations of its properties in whole world. The wide-ranging investigations of selenium and transformers on its base have begun in early 50^{th} in Institute of Physics of ANAS. The dependence of physical properties of selenium on external action conditions and impurities has the complex character. The many experimental data of different authors essentially differ that makes difficult their interpretation with unique positions. The ambiguity is caused by specificity and complexity of selenium structure, structure diversity of its molecules. This peculiarity gives to Se and its transformers on its base such property gamma which makes this semiconductor irreplaceable one in some cases. The same peculiarity transforms Se in difficult investigation object [1-4 and etc].

Se belongs to the number of more sensitive photosemiconductors in visible region of spectrum and that's why both amorphous and trigonal Se are widely used at formation of photoreceptors of different functional destinations.

EXPERIMENT AND RESULT DISCUSSION

The chemical methods of material obtaining and treatment have the big possibilities for directed change of photo-semiconductor properties. The fact that the final product is obtained more fine-dispersed one that at mechanical chopping and no necessity in separation by sizes is the one of important advantages of chemical method use. As only near-surface regions of photo-semiconductor particles take place in electrographic process (light quantums penetrate in intrinsic absorption region in depth 1μm), then the photo-semiconductor is used more effectively and the layers are more homogeneous ones at chemical method.

The photoreceptors on the base of amorphous selenium have the high electrographic parameters (good charging and sensitivity), but they have the essential disadvantages. They are weakly sensitive to red light, as a result of exploitation and even the storage the layers of amorphous Se crystallize under the influence of many factors and break down. Also, their production includes many steps, requires the difficult vacuum equipment, big power inputs and etc. Trigonal Se is known as photosemiconductor with spectral sensitivity covered whole visible region. Usually, layers of tetragonal Se are prepared by dispersing of its particles in polymer binding material and deposition of suspension on conducting substrate. They have well photosensitivity, but they have the low initial charging potential and dark semi-decay that is the sequence of Se high conduction.

Firstly, the aim of the given work is the defect elimination belonging to layers from trigonal Se obtained by usual dispersing technology in binding material·, and secondly, the search of improvement ways of their parameters and characteristics. With this purpose the search of appropriate chemical methods has been carried out.

The trigonal Se crystals are obtained from initial Se powder of high pureness 99,999%, by previous termo-treatment in evaporated quartz ampoules at 700^0C during 3 hours by rapid cooling of melt up to 250^0C, quenching in running water and crystallization at 210^0C during 40 hours (4). The specific resistance is

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$5 \cdot 10^6$ Om·cm with forbidden band thickness 1,8 eV. The melting point is 200^0C. The freshly prepared layers in binding material charge positively and have low charging potential. The monotonous annealing of layer main parameters is observed when the layers are treated to continuous annealing at 100^0C - 180^0C with further slow cooling. The general photosensitivity increases up to 0,5 $(\text{lux} \cdot \text{C})^{-1}$ at annealing 160^0C .

The chosen method of purification and doping of Se is caused by the following circumstances. It is known that impurities of alkali metals (for example, sodium) decreases Se conduction on several orders and that's why this should led to increase of layer charging potential on its base and decrease of its dark relaxation velocity. The advantage is in the fact that the photo-semiconductor material is obtained in the form of low-dispersed powder particles with the surface enriched by sodium in comparison with traditional high-temperature doping. The method is described in detail in work [5]: Se is endured during 5-16 hours in solution of caustic sodium with following neutralization by hydrochloric acid. The precipitated material is obtained in the form of low-dispersed powder particles of Se enriched by sodium. X-ray diffraction investigations show that Se obtained by the given method presents itself the low-dispersed powder of trigonal Se with average particle size ≤ 0,7 μm. The electrographic layers of them are prepared by dispersing in binding material from butyral resin solution in ethyl alcohol and deposition of suspension on electroconducting substrates. The layers with thickness 20 ± 2 μ m further are treated at 160^0C during 0,5 hours.

The main parameters and characteristics are investigated by noncontact method on electrometric installation with vibrating gauge under layer surface (in static regime). The electrization is carried out in corona charge by high voltage block ± 7kV) and exposure is carried out by white or monochromatic light. The irradiance is forecasted by radiation thermo-element. The decay of charging potential is registered by pointer instrument or storage unit C8-13 switched on to output of electrometric amplifier.

The general photosensitivity of electrographic layer is defined by decay velocity of charging potential at illumination. The photo-sensitivity criterion can be value of surface potential change at definite exposure conditions or exposition value necessary for providing of definite potential drop can serve the photo-sensitivity criterion. The layer photo-sensitivity can be characterized by time of exposure t (in seconds) duration which the surface potential decreases in two times in the case of L (in lux) constant illumination. At definition of spectral sensitivity, the illumination is measured in energy units by number of incident quantums on unit of area of layer surface per time unit. In case of L constant illumination the layer photosensitivity S_λ can be characterized by the time of exposure t (in seconds) duration which surface potential V decreases in two times:

$$S_\lambda = \left(\frac{1}{L\lambda * t}\right) \frac{\Delta N}{v} = \frac{1}{2}, \quad SM^2 \cdot J^{-1} \qquad (1)$$

The quantum efficiency of charge carrier photogeneration ή is defined as ratio of generated charge number in the layer Δn to number of absorbed light quantums ΔN. At illumination by monochromatic light potential decay ΔV is expressed by formula:

$$\Delta V = \frac{\Delta n * l}{C}$$

From here it is followed:

$$\acute{\eta} = \frac{\Delta n}{\Delta N} = \frac{\Delta V * C}{L * \Delta N} \qquad (2)$$

where C is layer electrocapacity, e is elementary charge. Using V, C,e and Δn we can calculate the spectral distribution of quantum output of internal photoelectric effect. After optimization of technological process of electrographic layer preparation the comparison of layer parameters of trigonal Se doped by sodium and initial one (without sodium) shows that the layers doped by sodium are the best on all parameters. This fact proves that chemical purification and doping by sodium essentially improves the layer properties on the base of trigonal Se in binding material. The method is in the fact that sodium impurities penetrate in near-surface region of trigonal Se micro-particles as a result of diffusion at annealing, i.e. especially in that region where light quantums penetrate at illumination of electrographic layer. Indeed, this is proved by the fact that general photosensitivity is bigger ($\geq 0{,}8$ $\text{lux}^{-1} \cdot \text{C}^{-1}$ at charging potential ≥300V) in layers of Se doped by sodium than in layers of initial Se. The essential outgrowing both photosensitivity and quantum output and also their expansion into long-wavelength spectrum region takes place in spectral distribution of photosensitivity and quantum output of the layers with doping. As quantum energy becomes enough for formation of electron-hole couples, then quantum output rapidly grows up to 0,7 and further the photo-sensitivity increasing up to 700 nm appears in absorption band. The illumination of intrinsic light (case of strong absorption) leads to photogeneration of charge carriers in thin near-surface region of electrographic layer whereas at impurity photo electric effect the carriers generate in whole volume. The photoreceptor has maximum photosensitivity in intrinsic absorption band. The general sensitivity decreases in the result of increase of forbidden band and intrinsic absorption edge shifts to the short-wave spectrum region. That's why for supply of its growth one should prepare the layer from photo-semiconductor with narrow band. So, the formation of electrographic layers on the base of trigonal Se is actual.

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