Optical Properties of Solar Thermophotovoltaic Elements Based on Three-Component Compounds Bi$_{2}$Te$_{3-x}$Se$_{x}$

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Abstract: The optical properties of Bi-Te-Se three-component semiconductor compounds are studied. The dependences of the light absorption coefficient in the Bi$_{2}$Te$_{3-x}$Se$_{x}$ film structures on the photon energy are studied. And, the effects of annealing on the dependence of optical parameters on the energy of photons are studied. It is shown that, the change in the light absorption coefficient is associated with significant variations in the composition of the films.

Keywords: Absorption, Semiconductor, Optical Properties, Solar Cells, Photon Energy, Temperature

1. Introduction

In recent years, significant progress has been made in the creation of solar thermophotovoltaic cells based on Bi-Te-Se three-component semiconductor compounds. The possibility of manufacturing various types of elements with heterojunctions using these compounds was proved. The Si - Bi$_{2}$Te$_{3-x}$Se$_{x}$ heterojunctions relate to the most promising structures that can be used to create photovoltaic converters stable for long-term operation, intended for large-scale energy production. Thin-film devices have very important properties, thanks to which the effective conversion of solar energy is feasible.

Among the main optical properties of three-component Bi$_{2}$Te$_{3-x}$Se$_{x}$ compounds, the strongest absorption of light at energies exceeding the width of the forbidden band attracts the most attention. Extremely high values of the light absorption coefficient allow reducing the requirements for the quality of the material and reducing the cost of solar cells. So, for example, to create an absorbing layer of Bi$_{2}$Te$_{3-x}$Se$_{x}$, a film with a thickness of less than 1µm is sufficient, so that the issues of the cost and availability of the material begin to play a less important role [1, 2]. A sharp edge of absorption at energy of 1.70eV corresponds to direct interband transitions. The existence of a different absorption edge at lower energies is due to carrier transitions from the level associated with the Bi vacancy to the conduction band. In n-type films, the second absorption edge is not observed, which confirms the theory that hole conductivity is due to Bi vacancies.

The efficiency of thermophotovoltaic conversion in thermophotovoltaic generators with selective filters based on known photoconverters reaches 25% at an emitter operating temperature of 1300°C. Perfection of photoconverters and radiators will increase the efficiency of thermo-photoelectric conversion. In thermal-photo-electric generators, solar radiation concentrators can be used as heat sources. In thermo-photo-electric generators, by means of elements sensitive in the near infrared region of the spectrum, thermal radiation is transformed into electric energy. This principle is known for a long time, and its practical implementation due to the development of highly efficient heterostructure photoconverters based on materials with a small bandgap and the creation of effective radiators with an operating temperature of 1000°C becomes possible only now. The composition of films of thermoelectric materials is primarily determined by the need to ensure a given concentration of charge carriers. The working concentration of charge carriers
in thermoelectric semiconductor materials ranged from $10^{18}$ to $10^{20}$ cm$^{-3}$. In order to provide such a concentration, a ratio should be maintained with an accuracy of at least 0.1 at%.

The concentration of electrically active point defects and foreign impurities should not exceed 0.1 at%. When preparing films of solid solutions of thermoelectric materials, such as Bi$_2$Te$_3$, the composition of the solid solution that determines the important thermoelectric parameters—the widths of the forbidden band, the effective mass of carriers and the thermal conductivity of the lattice, must be maintained. Photoconverters on the basis of these materials provide the efficiency of thermophotovoltaic transformation, exceeding 20%.

Si-Bi$_2$Te$_3$, heterojunctions were obtained by high-temperature annealing of samples. The control of the properties of the films directly in the process of their condensation makes it possible in a single technological cycle to form heterostructures with a given concentration of charge carriers. Films with the best parameters are obtained by spraying on a substrate at a temperature of 300°C, followed by annealing for 30 minutes. The density of electrical energy removed from photoconverters increases with increasing emitter temperature.

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As is known, in comparison with other types of autonomous power sources, thermoelectric photovoltaic generators have several advantages. Thanks to the creation of high-efficiency photoconverters and the radiators coordinated with them on the spectrum, the thermophotovoltaic generator will find wide application as autonomous sources of electric power in terrestrial conditions. The amount of electricity generated by a thermo-photovoltaic generator is approximately three times higher due to their continuous operation. The specific amount of electricity generated per unit area of photoconverters in thermoelectric photothermal generators is 100 times greater than in solar batteries.

2. Problem Statement

In thermophotovoltaic generators based on heterostructural $Si - Bi_2Te_3$, photoconverters it is possible to obtain a specific power of more than $3 \text{ W/cm}^2$. The efficiency of the system as a whole will be lower due to the loss of infrared radiation not absorbed in the semiconductor, the losses in the generation of thermal radiation and other heat losses. Losses can be minimized by converting radiation using selectively emitting emitters and filters reflecting long-wave radiation into the emitter.

Solar cells designed to work under concentrated light illumination belong to a special class of instruments, differing in many respects from elements used in conventional designs. Currently, work on the way to further increase the efficiency of solar photovoltaics working under conditions of moderate concentration of solar energy and minimizing the cost of the system as a whole is considered to be a priority.

The values of the short-circuit current and the no-load voltage, as well as the filling factor is determined by a number of factors. One of these factors can be called the presence of real solar cells of internal resistance. The nature of the internal resistance is insufficiently studied and is due to the resistance of the thickness of the material from both sides of the transition, as well as by the resistance of the face-to-face contact grid, which ensures the collection and transfer of current carriers to the load. The power is also lost due to the series resistance of the element as a whole.

With increasing intensity of irradiation monotonous growth of the photocurrent is observed. However, the open circuit voltage does not increase monotonically at a brightness of 4000 W/m$^2$, and then decreases, reaching a voltage value less than 1000 W/m$^2$. At the same time, the temperature of the structure under study increases with increasing illumination.

An increase in the value of the idling voltage in the first case is due to the effect of temperature, which has different effects on the main characteristics of the element - the magnitude of the potential barrier, the resistivity of the material of the contact mesh, and the resistance of the spreading of the antireflection coating. The growth and further decrease in voltage is the result of the competing interaction of several processes.

Figure 1 shows the dependence of the light absorption coefficient in several $Bi_2Te_3$ films on the photon energy. The curves show two features. A sharp edge of absorption at energy of $1.72\text{ eV}$ corresponds to direct interband transitions. The existence of a different absorption edge at lower energies is due to carrier transitions from the level associated with the $Bi$ vacancy to the conduction band. In n-type films, the second absorption edge is not observed, which confirms the theory that hole conductivity is due to $Bi$ vacancies [3-5].

In figure 2 show typical dependences of the absorption coefficient $\alpha$ on the photon energy for single-crystal and thin-film $Bi_2Te_3$ samples.

When approaching the absorption edge both in thin films and in crystals, a sharp change occurs, typical of semiconductors with direct interband transitions. At energies greater than the width of the band gap, $\alpha$ exceeds $10^7 \text{ m}^{-1}$. For several thin films, the values $\alpha=4*10^7$ - $7*10^7 \text{ m}^{-1}$ were obtained. They are the maximum among published values of $\alpha$ for any semiconductors, which agrees with very high short-circuit current densities ($410 \text{ A/m}^2$), typical for effective solar thermophotovoltaic thermal cells based on $Si - Bi_2Te_3$ [6-9].
Figure 1. Dependences of the light absorption coefficient $\alpha$ on the photon energy $h\nu$ in thin Bi$_2$Te$_3-x$Se$_x$ films deposited from two evaporators 1 - p-type film immediately after precipitation; 2 - n-type film immediately after deposition; 3 - film 2 after annealing in vacuum at a temperature of 380°C for 15 min.

Figure 2. Dependences of the absorption coefficient $\alpha$ on the photon energy in Bi$_2$Te$_3-x$Se$_x$ single crystals at a temperature of 320 K (1) and 100 K (2), as well as in thin films at 320 K (3).

The displacement of the curves of the dependence $\alpha$ (hv) along the energy axis corresponds to the data of other scientific papers. In most thin films, the edge of the main absorption band corresponds to energy approximately equal to $0.98eV$, and in single crystals $1.00-1.30eV$.

This can be due to several reasons. First, there is an electric field at the grain boundaries in polycrystalline materials. The absorbing properties of the material change under the influence of this field. However, this effect is usually observed for small values of a pin the tail region of the spectral characteristic $\alpha$ (hv). Therefore, it is unlikely that it is the main reason for the displacement of these characteristics relative to each other. Secondly, different samples of single crystals and thin films have a different chemical composition. The effect of temperature on the spectral characteristics of the absorption coefficient is illustrated in figure 2. When the temperature drops to 100K, the edge of the optical absorption corresponds to higher photon energy than its value at room temperature. The presence of a shift in the edge of the absorption band does not contradict the results of measurements of the temperature dependence of the band gap.

For the allowed direct interband transitions, the following relation between the absorption coefficient and the photon energy is valid:

$$\alpha h\nu = A (h\nu - E_g)^{1/2}$$

(1)

Here $A$ is a constant, and $E_g$ is the width of the forbidden band. Thus, for semiconductors in which the absorption of light is accompanied by direct interband transitions, the dependence $(\alpha h\nu)^2$ on (hv) has the form of a straight line. The position of its intersection with the photon energy axis characterizes the width of the forbidden band, as shown in figure 2 for several samples. At room temperature, single crystals and thin films (figure 2) are semiconductors with a direct band gap, whose width is $0.98$ and $1.00eV$, respectively. At a temperature of 100K, the width of the forbidden band of thin-film material increases largely than predicted by the theory, and reaches $0.99eV$. However, the most important circumstance is that the above dependences of the absorption coefficient on the photon energy indicate the existence of direct interband transitions.

Tails of the spectral characteristics of the absorption coefficient at small $\alpha$ are observed both in single crystals and in thin films [10, 11]. In these regions, the dependence of $\alpha$ on $h\nu$ is not described by equation (2). If interband transitions occur with the participation of phonons, then it takes the form.

$$\alpha = A (h\nu - E_g + E_p)^2/\exp(E_p/kT)-1)$$

(2)

Here $A$ is a parameter that does not depend on the photon energy, $E_p$ is the photon energy, and $E_g$ is the width of the forbidden band for indirect transitions. The curves for the dependences of $\alpha^{1/2}$ on $h\nu$ are shown in figures 3 and 4. The energies corresponding to the points of their intersection with the abscissa axis are consistent with the previously reported values of the wave number typical of optical phonons. These dependences (figure 3) used for their interpretation the theory of interband transitions with the participation of phonons.
Figure 3. Dependence on the energy of photons, indicating the additional absorption of light in the region of small values of the coefficient of extinction.

The energy values found by these authors are 0.016; 0.025; 0.044 and 0.054eV correspond to wave numbers that are characteristic of optical phonons. The absence of transitions at a low temperature also confirms that additional absorption of low-energy radiation is associated with transitions in which phonons participate.

The additional absorption of radiation by thin films for small values of $h\nu$ (figures 3 and 4) is not described by equations (1) and (2). The data presented here are typical for polycrystalline semiconductors, and the additional absorption of radiation is analogous to that in ZnS [12].

Figure 4. Dependences of $\alpha^{1/2}$ on photon energy in the region of low values of the absorption coefficient for crystals (1) and thin films (2) of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ at 300K.

Annealing in oxygen at a temperature of 150°C for 15min leads to a slight increase in the absorption coefficient at any photon energy, i.e., to an increase in the absorptivity of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$. This change in $\alpha$ is not associated with the growth of an oxide or any other surface film, since in the samples from the surface of which the oxide layer was removed by ion etching just before the measurement of the absorption coefficient, the values of $\alpha$ also increased. In deliberately oxidized samples, no such effect was observed. The thickness of the oxide layer, formed because of annealing at 200°C in pure oxygen, is usually 9...14nm. An analysis of the composition by the method of spectroscopy shows that the degree of heterogeneity in the distribution of atoms is reduced to below 0.3%. The dashed line corresponds to the original unannealed thin film. After heat treatment in oxygen, the absorption coefficient increases. The difference between the results, which lead to these two types of heat treatment, is insignificant. This is confirmed by the same increase in the short-circuit current of heterojunctions. However, heating the samples in a high vacuum causes a decrease in the absorption coefficient.

The release of selenium during the heat treatment is probably due to the relatively high vapor pressure of Se in the three-component compound. Consequently, the change in the absorption coefficient is associated in this case with significant variations in the composition of the films.

3. Conclusions

Thanks to the successful development of solar thermophotovoltaic cells based on $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, the other three-component $\text{Si} - \text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ compounds attract so much attention. Great interest in these semiconductors can contribute to their wider use as materials for the creation of photoelectric detectors and converters. Studies on the improvement of $\text{Si} - \text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ heterojunctions due to their undoubted potential capabilities will be sold.

References


