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Influence of annealing on photoelectric characteristics and stability of elements based on Si-$Bi_2Te_{3-x}Se_x$

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Abstract: In the manufacture of $Bi_2Te_{3-x}Se_x$-based elements using two sources of the deposited substance, they were initially annealed at a temperature of 150–200 °Ñ in a low vacuum. Heat treatment led to a slight increase in short circuit current and an increase in open circuit voltage. When the elements were heated in high vacuum, as well as in atmospheres of argon, nitrogen, hydrogen, helium and other gases, irreversible changes in the characteristics were not detected. Heat treatment of elements at a temperature of 100–150 °C in oxygen always improves their performance. It is assumed that annealing stimulates the growth of the transition layer at the interface. Annealing of solar cells based on Si-$Bi_2Te_{3-x}Se_x$ at an even higher temperature leads to a further irreversible deterioration of their characteristics.

Key words: Heterojunction, semiconductor materials, solar cells, converters, annealing

1. Introduction

An important technological operation in the production of highly efficient solar cells with Si-$Bi_2Te_{3-x}Se_x$ heterojunctions is heat treatment carried out after the deposition of semiconductor materials. They resorted to it even when developing thin-film devices. In the case of manufacturing elements based on $Bi_2Te_{3-x}Se_x$, it was initially carried out in the same way as when creating elements with the Cu_2S–CdS structure. All devices manufactured using two sources of the deposited substance were annealed at a temperature of 150–200 °Ñ in a low vacuum for 2–4 h. Such heat treatment, as a rule, led to a slight increase in the short circuit current and an increase of 10–15 mV open circuit voltage.

It has been suggested that, as a result of oxidation of the surface of an element, an unintended antireflection coating may form. This type of heat treatment was used by many researchers [1,2]. However, a significant improvement in the parameters of the devices is observed only during annealing in an oxygen-containing atmosphere. Studies of the back contact, performed using the high-resolution electron beam current induction method, led to somewhat unexpected results. For solar cells not subjected to heat treatment and annealed cells, the authors created a fracture surface and studied the distribution of the electric response in the plane of the cross-section [3–5].

2. Experimental details

The change in light and dark current-voltage characteristics is shown in Figure 1.

The effect of heat treatment on the dark characteristics of the same elements is illustrated in more detail in Figure 2. When heating solar cells in high vacuum, as well as in atmospheres of argon, nitrogen, hydrogen,

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*Correspondence: exmedovqurban@rambler.ru helium, and other irreversible gases no changes in characteristics were found. Heat treatment of elements at a temperature of 100–150 °C in oxygen always improves their performance.

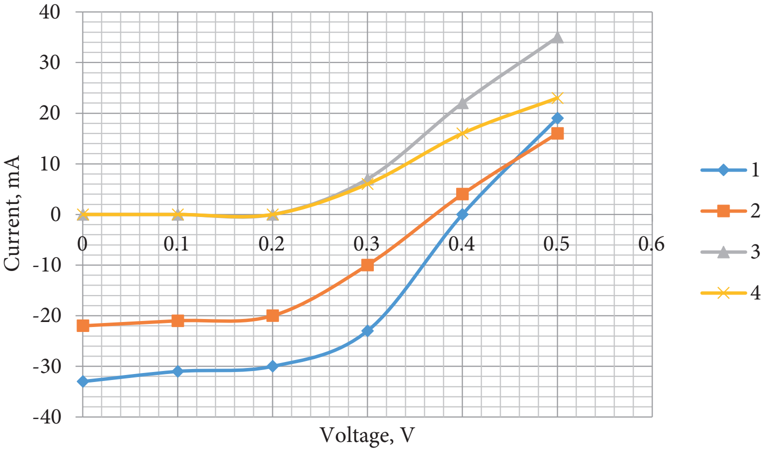


Figure 1. The effect of heat treatment in oxygen on the light (1,2) and dark (3,4) current-voltage characteristics of a solar cell with a Si-Bi$_2$Òå$_{3-}$Se heterojunction. Line 2: before annealing; line 4: after annealing.

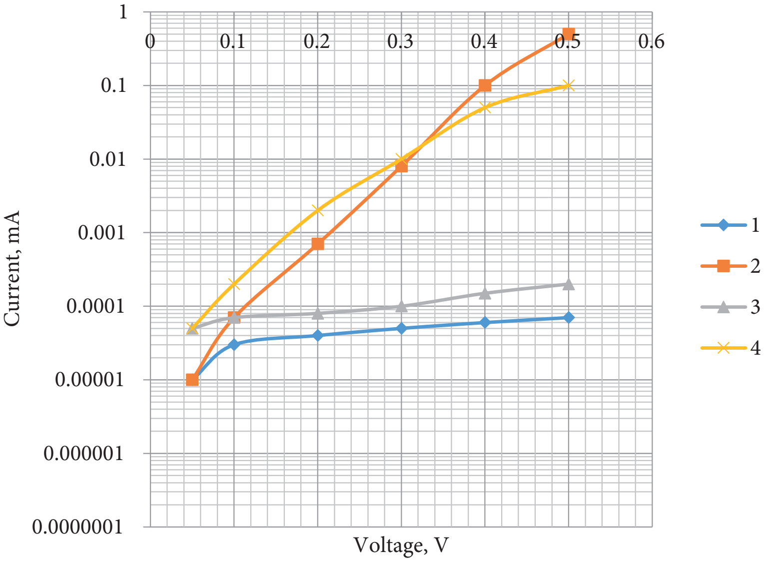
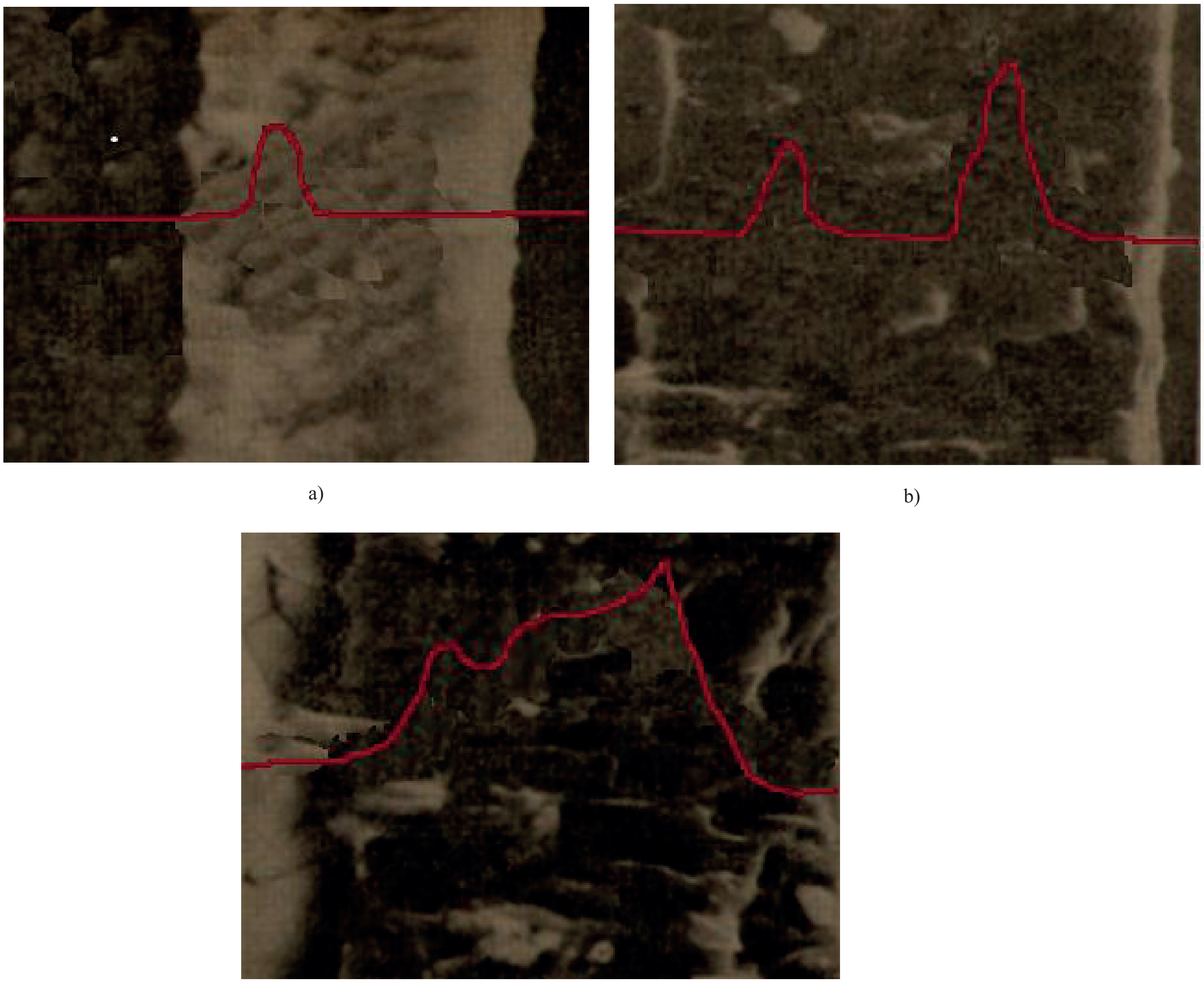


Figure 2. Dark current–voltage characteristics of solar cells with a Si-Bi$_2$Òå$_{3-}$Se heterojunction after heat treatment in oxygen (lines 1 and 2) and before (lines 3 and 4): lines 2 and 4 have a diode coefficient of 1.97, reverse current density saturation 1.2 ×10-1 A/m^2; lines 1 and 3 have a diode coefficient of 1.54, the density of the reverse current is 2.5 ×10-2 A/m^2.

All devices have little sensitivity in the area of the back contact due to the existence of a Schottky barrier between Mo and $\mathrm{Bi_2Te_{3-x}Se_x}$. For unannealed elements, the distribution of sensitivity in the heterojunction region is heterogeneous. This conclusion is confirmed by Figure 3, where the distribution of the current induced by the electron beam is presented along the scan line.

After annealing at a temperature of 150 °C for 2–3 h, the heterojunction (n-Si - p- Bi$_2$Òå$_{3-}$Se interface) is sensitized. According to available data, Bi$_2$Òå$_{3-}$Se immediately after deposition has a weakly expressed hole



a)

b)

c)

Figure 3. Distribution curves of the current induced by the electron beam in the plane of the cross section of a thin-film element based on Si-Bi$_2$Òå$_{3-}$Se : a) the presence of one signal associated with a potential barrier at the back contact Mo-Bi$_2$Te$_{3-x}$Se$_x$ of the unannealed element, b) the appearance of two signal from the heterojunction after annealing at a temperature of T = 150 °C for 20 min, c) the possible occurrence of additional three signal from the homojunction after annealing at T = 150 °C for 8 h.

or even electronic conductivity. Consequently, heat treatment in oxygen causes an inversion of the conductivity type Bi2Te3-xSex directly below the interface. Figure 4 shows the distribution curves of the current induced by the electron beam, which characterize the process of electroactivation, successively measured during vacuum annealing. If annealing is carried out in an oxygen-free atmosphere, then a significant increase in the efficiency of the elements does not occur. The change in the type of conductivity near the heterogeneous interface during heat treatment in various media (Ar, He, and vacuum) is also confirmed by the results of measurements of the capacitance-voltage characteristics.

After annealing at a temperature of 200 °Ñ, the capacitance increases significantly, which, according to the data obtained with the method of inducing current by an electron beam, is the result of electroactivation of the heterojunction (Figure 5, curve 1). Figure 5 shows the voltage dependence of the capacitance of an

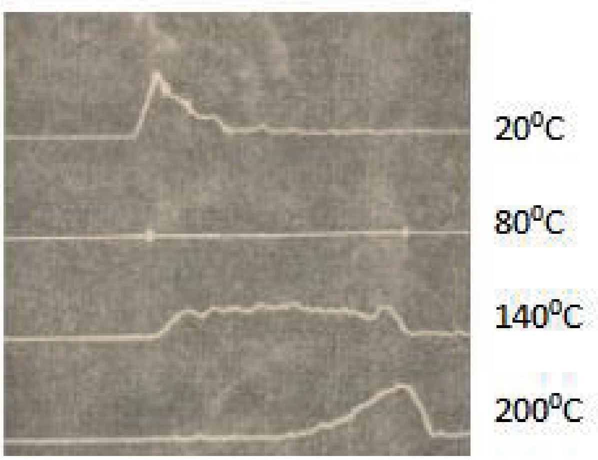


Figure 4. Distribution curves of the current induced by the electron beam in the plane of the cross-section of the solar cell during heat treatment in vacuum, combined with the image of the cleaved surface obtained using secondary electrons.

unannealed element measured at room temperature (curve 2). The capacity of this device remains almost unchanged with voltage variations. Warming up at a temperature of 150 °C slightly changes the capacitance-voltage characteristic (curve 3). In this case, $\mathrm{Bi}_2\mathrm{Òå}_{3-}\mathrm{Se}$ is almost completely depleted by free charge carriers and a Mott barrier forms. The positive sign of the derivative dÑ/dV indicates the formation of the p–n junction, which is possible with an inversion of the conductivity type. However, the role of oxygen in improving the characteristics of elements has not yet been precisely established. Most likely, it is not involved in changing the type of conductivity of Bi2Te3-xSex. As shown by studies by X-ray photoelectron spectroscopy, during heat treatment of samples in oxygen, a Bi-Se-O layer is formed on the Si surface, which reduces the specific resistance of Si. In addition to this, we currently have only limited information on the complex annealing process.

It is interesting to note that during a longer heat treatment; a homogeneous transition is also sensitized, which probably occurs at the interface between the p layers of low- and high-resistance $\mathrm{Bi}_2\mathrm{Òå}_{3-}\mathrm{Se}$. This can be seen from Figure 3, where the data are presented for an element subjected to heat treatment at a temperature of 150 °C for 8 h. Finally, another noteworthy feature of the annealing process is that the current induced in the Schottky barrier by an electron beam decreases with increasing duration of heat treatment, but the barrier does not completely disappear. Studies by X-ray photoelectron spectroscopy confirmed that in some elements MoSe2 or MoSe3 is formed on the back contact.

It is possible that it is these compounds that cause the observed changes in the height of the barrier at the back contact. To eliminate discrepancies between experimental data and theoretical results based on a simple heterojunction model, Kazmerski developed a heterojunction model with a p–i–n structure [6,7].

The existence of a Schottky barrier or a rectifying barrier of a different type at the back contact is confirmed by the experiments on inducing an electron beam in the current elements in the presence of a bias voltage. According to measurements of the induced current during illumination of elements using an additional radiation source, there is no light-induced barrier, although several research groups have suggested its existence [8-11].

Physical phenomena that make it possible to interpret the characteristics of elements with a $\mathrm{Si}\text{-}\mathrm{Bi}_2\mathrm{Te}_{3-x}\mathrm{Se}_x$ heterojunction and especially the role of final heat treatment remain the subject of discussion and increased

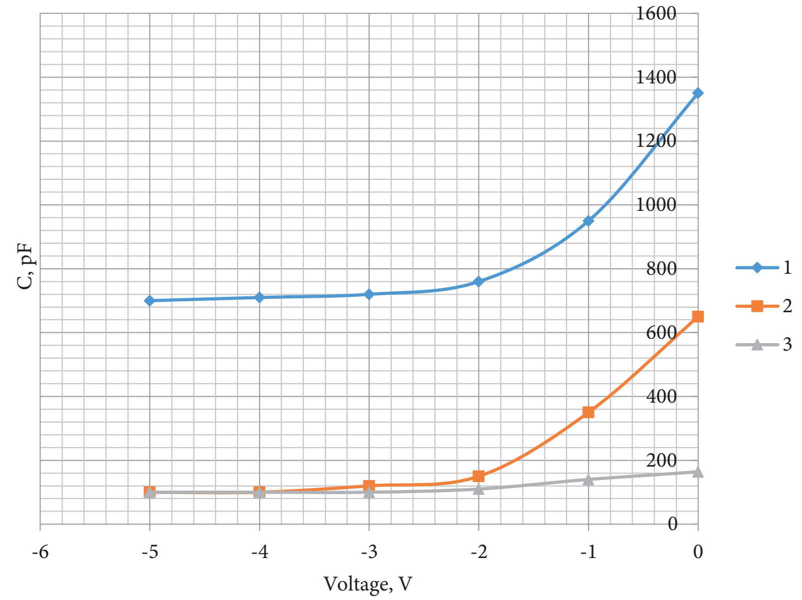


Figure 5. Capacitance–voltage characteristics of solar cells based on Si-Bi$_2$Òå$_{3-}$Se before 200 °C (1), heat treatment (2), and after annealing at temperatures of 150 °C (3). The measurements were carried out at a signal frequency of 1 MHz..

interest of researchers. The most important issues are related to the inversion of the conductivity type, the existence of light-induced transitions, oxygen diffusion, the formation and decrease of the height of the Schottky barrier or some other type of barrier at the back contact, sensitization of heterojunctions, measurements of the diffusion length of charge carriers, decrease in the resistivity of the optical window material, the influence of illumination, measurements of efficiency, etc. With so many problems, interest in solar cells based on Si-Bi$_2$Te$_{3-x}$Se$_x$ would undoubtedly have to cringe, if not for the fact that these devices in thin-film design have an efficiency of more than 10% and are characterized by extremely high stability in operation. To fully understand the processes occurring in solar cells of this type, extensive research is required.

The heat treatment of solar cells of the type under consideration is important not only as a means of optimizing the characteristics of already manufactured devices, but also as a process that allows obtaining information about their heat resistance. Establishing the relationship between the properties of the interface region and the operational characteristics of the elements reveals possible degradation mechanisms. Low-temperature annealing of solar cells based on Si-Bi$_2$Te$_{3-x}$Se$_x$ does not cause changes in their electrical characteristics and chemical composition of the interface. The output parameters of the element annealed at a temperature of 60 °Ñ in an argon atmosphere for 2 h and then cooled to 30 °Ñ are presented in Table. Significant changes in the parameters of the elements, including efficiency, are not noted. They are identical to the parameters observed after a longer exposure of the elements at a temperature of 60 °C. The profiles of the distribution of chemical elements over the thickness of the samples obtained by spectroscopy show that, at the indicated annealing temperature, the composition of the interface also does not change.

Changes in some electrical characteristics of the elements become significant at the annealing temperature 150 °C. The output parameters measured at 30 °Ñ for a solar cell subjected to heat treatment at a temperature of 200 °Ñ are also given in Table. Annealing time of 2 h in argon atmosphere. The 40% reduction in efficiency is due mainly to a decrease in short circuit current and a duty cycle of the current-voltage characteristic.

Table. The output parameters of solar cells based on Si-Bi$_2$Òå$_{3-}$Se at various heat treatment modes, measured at room temperature 28 °C and lighting, corresponding to AM1 conditions.

Availability of heat treatment	Open circuit voltage, V	Short circuit current density, A/m^2	Current-voltage characteristic fill factor	Efficiency, %
Before annealing	0.40	330	0.62	7.80
After annealing (50 °Ñ)	0.40	328	0.62	7.74
Before annealing	0.43	332	0.62	8.42
After annealing (200 °Ñ)	0.40	274	0.51	5.32
Before annealing	0.39	331	0.59	7.25
After annealing (300 °Ñ)	-	-	-	0

A similar increase in the width of the transition region, detected using depth distribution profiles of chemical elements, is also observed in devices made from polished Bi$_2$Òå$_{3-}$Se crystals. The interfaces between Bi$_2$Òå$_{3-}$Se single crystals and crystals previously studied by Wagner have similar properties [12].

These data suggest that annealing stimulates the growth of the transition layer at the interface. The presence of Si and Bi$_x$Se at this boundary can be judged by the results of the study by X-ray photoelectron spectroscopy.

Annealing of solar cells based on Si-Bi$_2$Òå$_{3-}$Se at an even higher temperature leads to a further irreversible deterioration of their characteristics.

The rapid diffusion of cadmium across the interface leads to the failure of the device. In addition, since cadmium diffusion in thin polycrystalline films is more intense than in single crystals, the mechanism of element degradation using polycrystalline substrates from ternary compounds is the diffusion of cadmium along grain boundaries. These results are consistent with previously obtained data on high-temperature processing of polycrystalline solar cells in which similar compounds are used [13–16].

3. Discussion and Conclusions

In recent years, significant progress has been made in creating solar cells based on three-component semiconductor bismuth compounds. The possibility of manufacturing various types of elements with homo- and heterojunctions using Si-Bi$_2$Te$_{3-x}$Se$_x$ is demonstrated. Si-Bi$_2$Te$_{3-x}$Se$_x$ heterojunctions are among the most promising structures that can be used to create photoelectric converters that are stable during long-term operation and are intended for large-scale energy production. Thin-film devices have the following three important properties, due to which the efficient conversion of solar energy is feasible.

The efficiency of the elements reached and then exceeded 10%, and at present they are the most efficient of the existing thin-film energy converters.

These converters unconditionally belong to the class of thin-film devices, since they have a total thickness of semiconductor layers of only about 6 µm.

As the initial results of testing the elements for stability under various conditions show, their characteristics do not change in the absence of sealing coatings.

The prospects for the future use of this type of device are determined by several factors. The first of these is the value of efficiency. It was previously believed that the use of thin-film solar cells is economically feasible provided that their efficiency is not lower than 10%. Recently performed calculations have shown that in reality it is necessary to have elements with an efficiency of 12–17%. An assessment of the potential capabilities of elements of this type indicates that an improvement in their characteristics is achievable. However, an increase in short circuit current cannot be expected, since its values ??are already approaching the maximum achievable. It is supposed to increase the open circuit voltage; the existing discrepancy between the values ??of this parameter in modern thin-film elements and their single-crystal analogs characterizes the possibilities of this improvement. Ongoing research and development of elements should provide highly efficient instruments.

Elements based on Si-$Bi_2Te_{3-x}Se_x$ are high-current low-voltage devices. There is reason to believe that due to the convenience of using high-voltage elements, they will be preferred in the industrial production of photovoltaic converters. This may necessitate the development of solar cell modules.

There is no certainty that the deposition of a semiconductor compound using three evaporators will eventually find application in large-scale converter manufacturing. However, none of the other known methods provides efficient solar cells. Extensive research on thin-film transducers should lead to their improvement.

Using this material raises some questions: is tellurium acceptable. Probably the cost of this material will be within acceptable limits. The analysis shows that the production of devices will be economical at a cost of tellurium of about 0.06$/W, which corresponds to the current level of prices for tellurium. Are the natural reserves of tellurium large enough? This is a very serious question, to which no definite answer can be given. The development of industrial methods for producing tellurium allows us to make optimistic forecasts, which, however, cannot be considered unconditionally fair.

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