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ELECTRIC PROPERTIES OF $p$-Cu$_2$ZnSn(S$_{1-x}$Se$_x$)$_4$/n-Si HETEROJUNCTIONS FOR THE CREATION NEW OF SOLAR CELLS

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Abstract
For the first time was obtained the anisotype heterojunctions $p$-Cu$_2$ZnSn(S$_{1-x}$Se$_x$)$_4$/n-Si by sulfurization of precursors previously deposited on a substrate of polycrystalline silicon. We analyze the current-voltage characteristics and discuss the current transfer in created structures. It is shown that tunnel-recombination processes, the tunnel mechanism and currents limited by space charge are typical for direct bias. Under reverse bias the transfer of currents carried by the tunnel and the tunnel-recombination mechanisms.

Key words: silicon, heterojunction, solar cells, semiconductor, current.

Introduction
Recently the interest in semiconductor heterojunctions has grown due to a number of their advantages compared to homojunctions. Heterojunctions (HJ) are widely used in electronics and photovoltaics [1, 2]. In manufacturing of solar cells (SC) based on HJ direct-gap semiconductors with large optical absorption capacity are used for the absorbent layer.

Semiconducting quaternary compounds Cu$_2$ZnSn(S$_{1-x}$Se$_x$)$_4$ (CZTSSe) are viewed as promising material for making absorbent layers in solar cells [3, 4]. CZTSSe is a direct-gap semiconductor with a wide band gap of 1.0 – 1.6 eV and has high absorption coefficient (>104 cm$^{-1}$ [4]) [3, 4]. Its components are widely accessible in nature, cheap and non-toxic. Over the last years based on compound CZTSSe solar cells’ efficiency has reached the level of 6.7% to 11.1% [3]. According to experts in the nearest 2-3 years the efficiency will reach 15%, and then the production of such solar cells’ will be launched [5]. Therefore CZTSSe is considered a promising material expected to replace indium-gallium compound in thin film solar cells.

For obtaining thin layers of CZTSSe various types of glass are used as substrate [6]. It should be noted that glass is not the most suitable material for substrate of solar cells based on CZTSSe. Firstly, glass is fragile material, which is especially pronounced in the synthesis of large size solar panels, the thickness of the glass substrate become 1 mm or greater, which significantly increases the weight of SC. Secondly, precision control is near impossible because of alkaline impurities in glass substrate. Alkaline impurities impair the reproducibility of the technological process.

CZTSSe based SC in the form of barrier transition typically includes HJ CdS/Cu$_2$ZnSn(S$_{1-x}$Se$_x$)$_4$ [4]. However, given the current environmental norms expulsion of toxic cadmium from SC becomes an urgent issue. Therefore there is a need to find an alternative way for CZTSSe based SC barrier transition.

Silicon is the most common semiconductor material in electronics and photovoltaics. 80% of all solar cells produced are based on it. However, the main challenge for reducing the cost of silicon based SCs is the high cost of obtaining monocrystalline silicon. Therefore it is important to utilize low-cost polycrystalline silicon. Efficient solar cells with p-n-junctions have been produced based on polycrystalline silicon [7]. In this regard it is interesting to study the electrical properties of HJ based on CZTSSe and polycrystalline Si.

In this paper we study the creation and electrical properties of anisotype $p$-Cu$_2$ZnSn(S$_{1-x}$Se$_x$)$_4$/n-Si heterojunction on a substrate of polycrystalline Si.

Methods
The experimental procedure for forming a thin layer 

$\text{Cu}_2\text{ZnSn(Se}_1-x\text{S}_x)_4$ (CZTSSe) on Si substrate was conducted in two stages. First, basic layers of components were formed on a substrate of polycrystalline Si by vacuum deposition method. The process was carried out under vacuum of $(3-5) \times 10^{-5}$ torr. The ratio of components in the initial sample was taken in accordance with the stoichiometric composition of the compound. In the second stage of the process sulfurization of the metal layers was conducted from unlimited source in a closed ampoule. To do this, samples of polycrystalline Si with deposited components were placed in a quartz ampoule evacuated to $(1-3) \times 10^{-5}$ torr. To ensure uniform sulfurization and prevent evaporation of sulfur from the forming film, sulfur was placed in the ampoule in the amount that supports the necessary pressure inside. The process of forming CZTSSe film was conducted by thermal annealing of samples with base layers in a technological furnace. To study the formation of CZTSSe films on Si, the components were deposited both sequentially and simultaneously, besides in sequential deposition of components the sequence was varied. The film thickness after each deposition stage was controlled by metallographic method. Samples were subjected to thermal annealing at temperatures of 450–600°C, while the annealing time was set in the range of 30-60 minutes.

Results and findings

Studying the morphology of grown films under different procedures showed that more smooth surface is received by spraying the components in the sequence of tin - zinc - copper and annealing at temperatures of 540-550°C. In other deposition sequences of components and higher annealing temperatures there forms some asperity that is apparently due to volatilization of certain components of the compound. With this in mind, further annealing of the samples was carried out at temperature of 550°C.

The spectra of x-ray reflections of CZTSSe films have been analyzed, and they showed polycrystalline structure of films with crystallite grain oriented mostly along the directions (112). The microstructure of the films showed that the crystallite grain sizes depend on annealing temperature and quenching mode. With increasing annealing temperature and decreasing rate of cooling of samples one observes increase in the size of the crystallite grains.

We measured the electrical parameters of the films. All samples obtained without special doping had p-type conductivity. Apparently during the formation of CZTSSe films some structural defects appear such as absence of copper atoms (V$_{Cu}$) and substitution of zinc knot with copper (Cu$_{Zn}$). V$_{Cu}$ ionization energy is ~ 0.02 – 0.08 eV, ionization energy of Cu$_{Zn}$ ~ 0.10 - 0.15 eV [8]. These defects with shallow acceptor levels determine the type of conductivity of the formed films. The surface resistance of CZTSSe films was within 25-50 Ω/sq.

We measured stationary current-voltage characteristics (CVC) of the created p- Cu$_2$ZnSn(Se$_1-x$S$_x$)$_4$/n-Si heterojunctions at room temperature. The ohmic contacts to the structures were obtained by placing eutectic alloy of indium-gallium. Forward and backward branches of the current-voltage characteristics I(U) of the heterostructure are shown in Fig. 1. The figure shows that the heterostructure diode has distinct characteristics.

Moreover, the direction of flow in all HJ is observed when applying positive polarity external bias on CZTSSe films, which is consistent with the zone models of HJ under study [9]. Rectification coefficient in the best structures at $|U|$ = 1-2 V reached the levels of K = 55-85. The resulting relatively small values of K are most likely to be related to the imperfection of heterojunctions’ transition region.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Fixed CVC p-Cu$_2$ZnSn(Se$_1-x$S$_x$)$_4$/n-Si heterojunction at T = 300 K.}
\end{figure}

In the forward voltages $U < 0.15$ V (Fig. 2, Curve 1) direct current increases exponentially according to the following:

$$I = I_s \exp\left(eU/nkT\right),$$

where $I_s$ is saturation current, and $n$ is Diode indicator. Evaluation of variables yielded the following results:
Is = (1,1-3)×10^{-7} \text{ A}, n = 1,7-2,5 \text{ at } T = 300 \text{ K}. \text{ The analysis of these values indicates that at low voltages in HJ current transfer mechanism is likely to be tunnel - recombination one.}

As can be seen from Fig. 3 (curve 1) at forward voltages 0,15 <U<1,2 V the current follows I \sim U^{m}. \text{ The value of the exponent } m \text{ for various structures was within 1,0–1,2. It shows, that for the current transfer are responsible either the mechanism of tunneling or the currents limited to a spatial charge in a mode of saturation of speed of carriers of a charge. At voltages 1,2 <U<2,0 V the value of the exponent increases to two. This points at the prevalence of current limited by space charge in mobility mode [10, 11]}

\[
I = (8\varepsilon\varepsilon_0\mu R S/d^3) U^2, \tag{2}
\]

where \( \varepsilon \) is dielectric permeability of CZTSS, \( \varepsilon_0 \) – dielectric permeability of vacuum, \( S \) area of the the heterojunction, \( d \) is the thickness of the substrate. Fig. 1 shows that the direct branch of CVC p-Cu\textsubscript{2}ZnSn(Se\textsubscript{1-x}S\textsubscript{x})4/n-Si at voltage U>2 V is subject to the following linear relationship

\[
U = U_0 + I R_b, \tag{3}
\]

where \( U_0 \) is voltage cutoff and \( R_b \) is base resistance. For p-Cu\textsubscript{2}ZnSn(Se\textsubscript{1-x}S\textsubscript{x})4/n-Si heterojunction their values were 1,8–2,0 V and (0,28–0,35) 10^3 \Omega respectively. Volatility of base resistance within fairly wide range is likely to be associated with changes in the conditions of CZTSSe films' crystallization.

\[\text{Fig. 2. Stationary CVC of p-Cu}_2\text{ZnSn(Se}_{1-x}\text{S}_x)_4/n-Si HJ in semi-log scale: 1-forward branch; 2- backward branch at } T = 300 \text{ K.}\]

\[\text{Fig.3. Forward (1) and backward (2) of CVC p-Cu}_2\text{ZnSn(Se}_{1-x}\text{S}_x)_4/n-Si heterojunction in double-log scale at } T = 300\text{K.}\]

At reverse bias of p-Cu\textsubscript{2}ZnSn(Se\textsubscript{1-x}S\textsubscript{x})4/n-Si relationship between current and voltage also follows I \sim U^{m} across wide range of voltages. As it can be seen from Fig. 3 (curve 2) backward branches of CVC can be divided into two sections. For values of │U│<1,0 V CVC is described by expression I \sim U^{m} (m=0,9-1,1). In this voltages for the current transfer is responsible the mechanism of tunneling. When the voltage 1,0<│U│<4,0 V the reverse current increases exponentially according (1). Evaluation of variables yielded the following results: 1_s = (0,7-1,0) \times 10^{-5} \text{ A}, n = 6,3–6,8 \text{ at } T=300 \text{ K}. \text{ The analysis of these values indicates that at voltages 1,0<│U│<4,0 V in HJ current transfer mechanism is likely to be tunnel – recombination one. At voltages │U│> 4,0 V soft breakdown has been begin.}

\[\text{Conclusion}\]

We for the first time obtained anisotypic p-Cu\textsubscript{2}ZnSn(Se\textsubscript{1-x}S\textsubscript{x})4/n-Si heterojunctions through sulfurization of preliminarily deposited metal layers on a substrate of polycrystalline silicon. Smoother surface of CZTSSe films are obtained by spraying the components in the sequence tin - zinc - copper and annealing at temperatures of 550^0 C.

The analysis of CVC of p-Cu\textsubscript{2}ZnSn(Se\textsubscript{1-x}S\textsubscript{x})4/n-Si established dominant current transfer mechanisms. At low forward voltages (U<0,15 V) tunnel-recombination mechanism is likelier to areas in heterojunction. At voltages 0,15< U<1,2 V in heterojunctions dominated the tunnel mechanism and at voltages 1,2< U<2 V currents are limited by space charge.
For voltages $U>2$ CVC varies linearly.

In reverse bias until $U = 1.0$ V for the current transfer is responsible the mechanism of tunneling, in the voltage $1.0 < |U| < 4.0$ V current transfer mechanism is tunnel-recombination processes. At voltages $|U| > 4.0$ V soft breakdown has been begin.

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