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Analysis of the Influence of Annealing Temperature on Mechanisms of Charge Carrier Transfer in GaAs in the Aspect of Possible Applications in Photovoltaics

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The article presents the results of investigations of the mechanisms of electric charge transfer in gallium arsenide subjected to poly-energic implantation with hydrogen ions, as a potential base material dedicated for photovoltaic applications. The main objective of the research was to determine the relationship between the temperature of isochronous postimplantation annealing and the probability of electron jumping between energy levels as a function of operating temperature and to test the possibility of creating additional intermediate energy levels in the semiconductor band gap by ion implantation, which in practice could allow increase in the efficiency of solar energy conversion in photovoltaic cells made on the basis of gallium arsenide modified by ion implantation technology. The conducted research allowed to identify two additional energy levels with activation energy values of 0.17 eV and 1.1 eV.

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1. Introduction

Based on the literature reports it is commonly known that many types of photovoltaic panels and technologies of their production are currently available on the commercial market, such as silicon (amorphous, crystalline), cadmium telluride (CdTe) and cadmium sulphide (CdS), organic and polymer cells, hybrid photovoltaic cell, thin film technology [1]. The most popular material used in the production of photovoltaic cells is silicon. According to the latest report of U.S. National Renewable Energy Laboratory on the best research-cell efficiencies [2], the maximum efficiency of the single crystal silicon photovoltaic cells reaches the level of 25%.

On the other hand, the same report indicates the gallium arsenide as the material that enables to increase substantially the efficiency of PV cells up to 44.7%. However, considering the current state of the art, improving performance of GaAs cells requires a multithreaded approach that concentrates on reducing many different loss factors which affect final efficiency of the cell. Among them, it is possible to distinguish electrical, optical, and quantum losses, as it was reported in [3, 4]. In particular, the quantum loss factor is strictly connected with the internal structure of the cell substrate. Especially, the value of the band gap determines energy that incident photon has to possess to be absorbed by the material and participate in the photoconversion process. For that reason, there is a strict correlation between the solar cell efficiency and the value of the band gap [5]. This value is typical of specific materials, e.g. the band gap of GaAs is approximately 1.43 eV. Nonetheless, by introducing some modifications of the GaAs crystal lattice, it is possible to control the arrangement of the energy bands as well as width of the band gap. It is commonly known that application of ion implantation technology enables to create additional energy levels in the band structure. What is more, changing implantation conditions allows controlling the character of introduced levels precisely [6, 7].

The role of ion implantation technology in the solar cell substrates manufacturing process was also discussed in Ref. [8]. On the other hand, in the papers [9] the influence of proton implantation and post-implantation annealing on the physical properties of GaAs substrate was explained. The key aspect is the analysis of the mechanism of electric charge transfer in the areas affected by ion implantation and determination of the probability of leap between the energy levels. The model of jump mechanism of electric charge transfer for both direct and alternating currents was presented in the papers [10, 11]. The described model introduces an assumption that an electron jump takes place between the neutral potential wells which causes formation of a dipole. The electron would be able to participate in direct current if only it makes another jump from the negative potential well in the direction opposite to the electric field vector. However the electric field of positively charged potential well from which the first jump was made withstands the succeeding jumps. One of the basic parameters of the model is probability of the second electron jump p. Probability that the electron will return to the first potential well equals $(1-p)$ and defines conductivity for high frequencies.

Considering the above, and taking into account the results of investigations concerning of silicon, implanted with Ne^{+} ions presented in [12] in combination with the methods for reduction of photoconversion losses

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described in [3], it can be argued that by using poly-energetic hydrogen ion implantation to modify the electrical properties of GaAs and using the above-mentioned mechanism of jump conductivity, it is possible to generate and identify additional intermediate energy levels in the band gap and consequently improve the photoconversion efficiency of the modified GaAs, as a base material for photovoltaic cells. In this article, the thesis is shown in an experimental way.

2. Experiment

In order to determine the probability of charge hopping in the ion-implanted semiconductors, the GaAs type n crystals produced using the Czochralski method were tested with the following parameters: thickness (400 ± 20) μm, resistivity (0.55 ± 0.05) Ω cm, concentration of carriers $(2.7 \pm 0.4) \times 10^{15}$ cm^{-3}, mobility of carriers 4180 cm^2 V^{-1} s^{-1}, orientation $\langle 100 \rangle$. Before implantation, the resistive contacts on both sides of the test sample were applied to the plate using the method of temperature vapour deposition of the multilayer vacuum structure. The multilayer structure formed in this way was annealed at 663 K in the hydrogen atmosphere creating ohmic contacts. The samples prepared in this way were subjected to the poly-energy implantation with the hydrogen ions of the following, selected by means of computer simulation. In order to determine sets of energy and doses, optimal for the production of flat depth profiles of defect concentration radiation caused by poly-energy ion implantation, the PROFCON calculation algorithm described in [13] was used. The algorithm used was based on the solution of the Fredholm's first type equation. Discrete dose values were determined by integrating continuous energy spectrum in selected ranges of energy values. The basic energy values were selected in such a way that the neighboring defect concentration profiles are homogeneous in depth and overlap to a sufficient degree. The following energy and dose values were determined: 65 keV — 1×10^{14} cm^{-2}, 130 keV — 1.1×10^{14} cm^{-2}, 220 keV — 1.2×10^{14} cm^{-2}, 300 keV — 1.5×10^{14} cm^{-2}, 400 keV — 2×10^{14} cm^{-2}. The tests included recording the conductance and capacitance at the ambient temperature T_p from 77 K to 373 K with 5 K step. The frequency f of the measurement signal ranged from 50 Hz to 5 MHz and the bias voltage was equal to 0.4 V. The samples were subjected to 15 min. isochronous annealing, in the T_a temperature range up from room temperature (without annealing) to 663 K, with an average increase rate of $(30 \div 50)$ K. Details of the measurement methodology, description of the test stand and software used were described in [14].

3. Analysis of the obtained results

According to the model of electric charge transfer mechanism for both direct and alternating currents, described in detail in [7, 15–17], the dependence of electrical conductivity on testing frequencies changes as follows. In the low (L) and high (H) frequency conductivity satisfies the condition

$$\sigma_L \approx \mathrm{const}_1, \quad \sigma_H \approx \mathrm{const}_2, \tag{1}$$

and, additionally, the value of probability p satisfies the equation

$$p = \frac{\sigma_L}{2\sigma_H}. \tag{2}$$

Within the range of medium testing frequencies the following proportion is fulfilled

$$\sigma_M \sim f^{\alpha}, \tag{3}$$

where $\alpha \leq 2$ is the frequency coefficient of conductivity, f is testing frequencies.

Figure 1 presents the dependences of conductivity on the testing frequencies conductivity $\sigma(f)$ for the GaAs sample irradiated with H^+ ions. The presented plots were registered for different values of the testing temperature T_p and for tested sample annealing temperature T_a of 663 K.

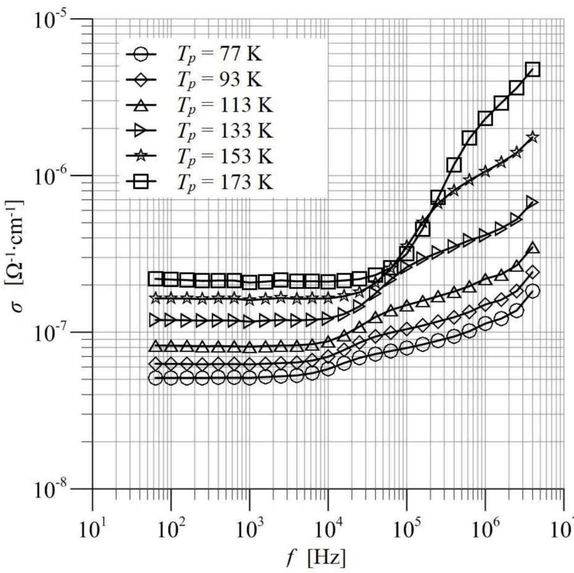

Fig. 1. Conductivity σ of the sample GaAs vs. testing frequency f for annealing temperature $T_a = 663$ K and for different values of testing temperatures T_p.

The dependences of coefficient α on the testing frequency are shown in Fig. 2 and refer to the same experimental conditions as the plots presented in Fig. 1.

As it could be seen in Fig. 1, within the domain of low $(f < 1 \times 10^4$ Hz) and high $(f > 5 \times 10^5$ Hz) frequencies, the values of conductivity satisfy the condition (1). In the area of transitional frequencies the increase of σ could be observed up to the proportion (3). In addition, value of the frequency coefficient α attains the maximum (Fig. 2). On the basis of the data in Fig. 1 and similar graphs plotted for the other annealing temperatures T_a, some calculations were made in accordance with the formula (2). As a result, the correlations between the probability p and the inverted temperature $(1000/T_p)$ were formulated [6].

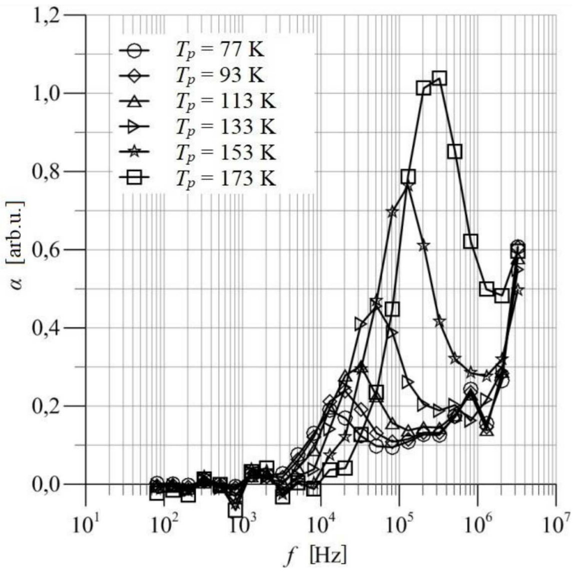

Fig. 2. Frequency coefficient α of the sample GaAs vs. testing frequency f for annealing temperature $T_a = 663$ K and for different values of testing temperatures T_p.

Figure 3 shows such dependences determined for the GaAs sample irradiated with the poly-energy H^+ ions. The plots in Fig. 3 could be divided into three groups. The dependences referring to the sample annealing temperatures $T_a \leq 473$ K could be included into the first group. Within the range of these annealing temperatures the plots $p(1000/T_p)$ reveal a decreasing tendency. Each of them consists of two parts which differ with respect to their inclination angle.

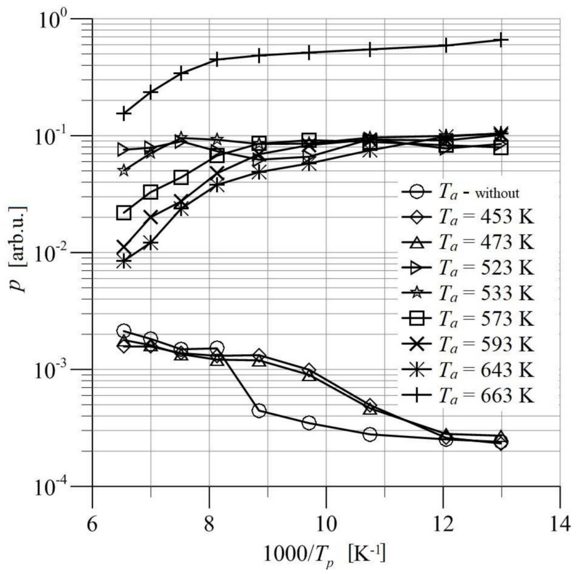

Fig. 3. Probability p versus inverted testing temperature $1000/T_p$, for different values of annealing temperatures T_a.

Annealing of the tested sample in the temperature range 523 K $\leq T_a \leq$ 643 K (which determines the second group of plots in Fig. 3) caused, firstly, a rapid increase in the value of p. Secondly, a tendency of changes of $p(1000/T_p)$ correlation gone upward instead of downward. In this group every plot can be also very clearly divided into two parts with different inclination, alike to the first group.

In the third group for $T_a \approx 663$ K another rapid growth of the value of p takes place whereas the plot shape is similar to that obtained in the second group. Such dynamics of $p(T_a)$ dependency changes could be explained by the changes in the conductivity value revealed during the annealing process.

Figure 4 shows the annealing temperature T_a of the GaAs sample which has influence on transfer electric charges probability. These changes could be observed for the annealing temperatures T_a at about 500 K and 650 K. Within this range of T_a it is possible to observe a significant increase in the value of probability p, from 1×10^{-3} arb.u. to 1×10^{-1} arb.u. Such situation is connected with annealing of two different kinds of radiation defects, which introduces such energy levels as $\Delta E_1^L \approx 0.17$ eV (for $T_a > 473$ K) and $\Delta E_2^L \approx 1.1$ eV (for $T_a > 643$ K) into forbidden energy band.

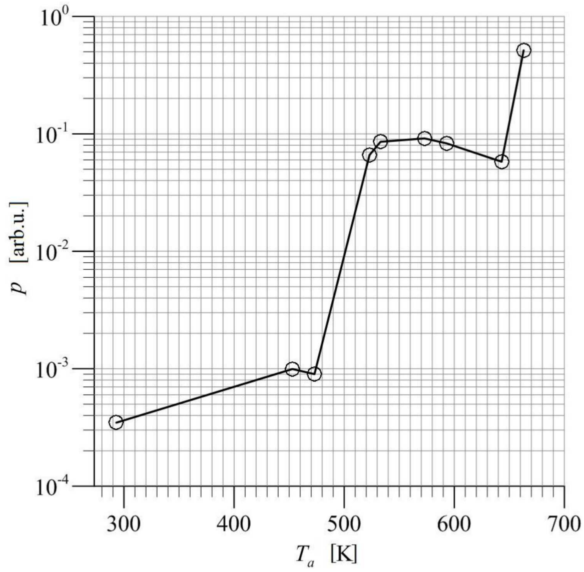

Fig. 4. Probability p versus annealing temperatures T_a, determined for the GaAs sample type n irradiated with poly-energy H^+ ions for testing temperatures $T_p = 103$ K.

4. Conclusions

The paper discusses the correlations between the electron jump probability p and the annealing temperature T_a. It allows to conclude that the observed value of probability is strictly connected with the type of radiation defects. Fading of every single defect during the annealing process causes rapid changes of the value of electron jump probability p. The conducted research allowed to identify two additional energy levels in the band gap with activation energy values of 0.17 eV and 1.1 eV.

The mechanisms of transferring electric charges in the semiconductor band gap width identified in the paper and the methods of determining the probability of charge hopping between the additional energy levels resulting from the H^+ ions implantation can find practical applications in increaseing the efficiency of photovoltaic cells based on gallium arsenide.

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