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Application of poly-energy implantation with H^+ ions for additional energy levels formation in GaAs dedicated to photovoltaic cells

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Abstract: The aim of this article is to present the results of research aimed at confirmation whether it is possible to form an intermediate band in GaAs implantation with H^+ ions. The obtained results were discussed with particular emphasis on possible applications in the photovoltaic industry. As it is commonly known, the idea of intermediate band solar cells reveals considerable potential as the most fundamental principle of the next generation of semiconductors solar cells. In progress of the research, a series of GaAs samples were subjected to poly-energy implantation of H^+ ions, followed by high-temperature annealing. Tests were conducted using thermal admittance spectroscopy, under conditions of variable ambient temperature, measuring signal frequency in order to localize deep energy levels, introduced by ion implantation. Activation energy ΔE was determined for additional energy levels resulting from the implantation of H^+ ions. The method of determining the activation energy value is shown in Fig. 2 and the values read from it are $\sigma_0 = 10^{-9}$ $(\Omega\cdot\text{cm})^{-1}$ for $1000/T_0 = 3.75$ K^{-1} and $\sigma_1 = 1.34 \times 10^{-4}$ $(\Omega\cdot\text{cm})^{-1}$ for $1000/T_1 = 2.0$ K^{-1}. As a result, we obtain $\Delta E \approx 0.58$ eV. It was possible to identify a single deep level in the sample of GaAs implanted with H^+ ions. Subsequently, its location in the band gap was determined by estimating the value of ΔE. However, in order to confirm whether the intermediate band was actually formed, it is necessary to perform further analyses. In particular, it is necessary to implement a new analytical model, which takes into consideration the phenomena associated with the thermally activated mechanisms of carrier transport as it was described in [13]. Moreover, the influence of certain parameters of ion implantation, post-implantation treatment and testing conditions should also be considered.

Key words: energy levels, gallium arsenide, intermediate band solar cells, ion implantation, thermal admittance spectroscopy

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1. Introduction

It is commonly known that many types of photovoltaic panels and technologies of their production are currently available on the commercial market. In the last decade, it was possible to notice a thriving development of this branch of industry, especially a trend to continue searching for new materials and production methods, aimed primarily at improving the efficiency and reducing the price of PV cells. The most common and most popular material used in the production of photovoltaic cells is silicon, because of such advantages as low price, widespread accessibility and high stability of crystal structures. According to the latest report of U.S. National Renewable Energy Laboratory on the best research-cell efficiencies [1] 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 substantially increase the efficiency of PV cells up to the 44.7%. What is more, in the works [2, 3] it has been shown that single-crystal, thin-film GaAs PV modules have achieved higher efficiencies than their polycrystalline and amorphous counterparts. In addition, authors of [4] reported that low-cost manufacturing processes are being developed by reusing the single-crystal substrates. Additionally, announcing the results of the experimental measurements, authors of [5] concluded that a recently tested non-concentrator GaAs PV module operates with the efficiency level which is nearby the theoretical limit and it is expected to be less sensitive to the influence of the operating temperature.

However, considering the current state of the art, improving the performance of GaAs cells requires a multithreaded approach that concentrates on reducing many different loss factors, which affect the final efficiency of the cell. Among them, it is possible to distinguish electrical, optical and quantum losses, as it was reported in [6]. In particular, the quantum loss factor is strictly connected with the internal structure of the cell substrate. Especially, value of the band gap determines the energy that an 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 solar cell efficiency and the value of the band gap [7]. This value is typical for 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 the width of the band gap. It is commonly known that the application of ion implantation technology enables to create additional energy levels in the band model. What is more, changing implantation conditions allows controlling the character of introduced levels precisely [8]. In such circumstances, the question arises whether this phenomenon could be used to improve the performance of GaAs-based PV cells.

The role of ion implantation technology in solar cell substrate manufacturing process was also discussed in article [9]. On the other hand, in papers [10, 11] the influence of proton implantation and post-implantation annealing on the physical properties of the GaAs substrate has been explained. In our previous work [12] formation of a single deep level in the sample of antimony-doped silicon implanted with Ne^{+} ions was investigated. The aim of this article is to confirm whether it is possible to use this substrate to form multiple deep levels of character that would improve absorption of photons, ensuring the possibility of taking advantage of the created structure on the way to increase silicon solar cells efficiency.

2. Methodology

The main aim of the research was to verify if it is possible to create the intermediate energy levels in GaAs by poly-energy implantation H^+ ions. The purpose of the performed experiment was to determine optimal implantation and post-implantation treatment conditions in order to achieve maximum stability of the measured values of conductivity σ and capacity C in the function of operating temperature T_p and annealing temperature T_a. The experiment has been carried out in accordance with the methodology described in [8, 13, 14]. The research was based on gallium arsenide produced by the Czochralski method with a $\langle 100 \rangle$ orientation, type n conductivity, with a tellurium dope, and initial resistivity $\rho = (0.55 \pm 0.05)\ \Omega \cdot \mathrm{cm}$, the concentration of current carriers $n = 2.7 \pm 0.4 \cdot 10^{15}\ \mathrm{cm}^{-3}$ and mobility $\mu = 4180\ \mathrm{cm}^2/\mathrm{Vs}$. In order to generate low-level contact on the semiconductor under test, a eutectic alloy layer (88% Au, 12% Ge) 0.15 µm thick was applied on both sides, followed by a 0.5 µm thick Ni layer and finally a 0.1 µm Au layer. In addition, the Au layer, 1 µm thick, was applied unilaterally (from the non-implanted side). In order to obtain the regular distribution of dopant, the tested samples have been subjected to poly-energy implantation of H^+ ions of energies $E = 65$, 130, 220, 300 and 400 keV and respective doses $D = 10^{14}$, 1.1×10^{14}, 1.2×10^{14}, 1.5×10^{14} and $2.0 \times 10^{14}\ \mathrm{cm}^{-2}$. The performed measurements covered the operating temperature range from 77 K to 433 K. During the experiment, samples have been isochronously annealed for 15 min, within the range of annealing temperatures T_a up to 663 K, with an average increment of (20÷40) K.

All the tests were carried out at the station shown in Fig. 1 and described in detail in the paper [15].

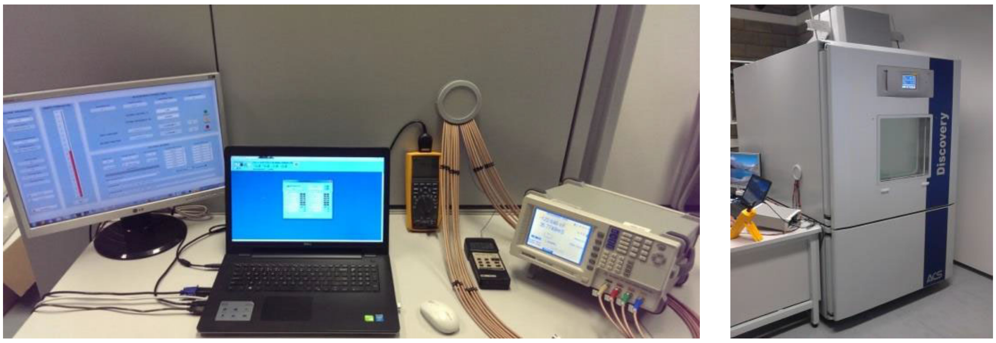

Fig. 1. Laboratory stand for identification of deep energy levels in GaAssubjected to ion implantation

3. Analysis of obtained results

Measurements of electric parameters of n-type gallium arsenide implanted in poly-energetic H^+ ions were carried out according to the above-described methodology in the temperature range T_p from liquid nitrogen LNT to 433 K for different heating temperatures T_a (without heating, 453 K, 523 K, 593 K, 643 K, 663 K) and measuring frequencies $f = 10^3$; 10^4; 10^5; 10^6 Hz. This allowed making the characteristics $\sigma = f(1000/T_p)$ on the basis of which the ΔE was calculated using Formula (2).

It should be noted that in the semiconductor understudy in the whole temperature range, various types of radiation defects coexist with different depths of the potential well, which causes that the characteristics $\sigma = f(1000/T_p)$ of the components derived from radiation defects of approximately ΔE "overlap" each other. Therefore, additional energy levels were only determined for those places on the characteristics $\sigma = f(1000/T_p)$, where the measuring points formed a straight line of a minimum in the range of several dozen Kelvin.

On the basis of the results obtained, characteristics were made for all options of $\sigma = f(1000/T_p)$. In contrast, Fig. 2 and Fig. 3 show only exemplary dependencies for $T_a = 523$ K, This example illustrates a method for determining the activation energy corresponding to an additional energy level in a semiconductor band, made by means of ion implantation. The results obtained for the remaining heating temperatures T_a and the measurement frequencies f are given in Table 1. Assuming that the conductivity varies with the temperature according to the Arrhenius formula:

$$\sigma = A \cdot e^{-\frac{\Delta E}{kT}}, \tag{1}$$

where: k is Boltzmann's constant; T is the temperature; ΔE is the activation energy, we get:

$$\Delta E = \frac{k \cdot \ln \dfrac{\sigma_1}{\sigma_0}}{\dfrac{1}{T_0} - \dfrac{1}{T_1}}. \tag{2}$$

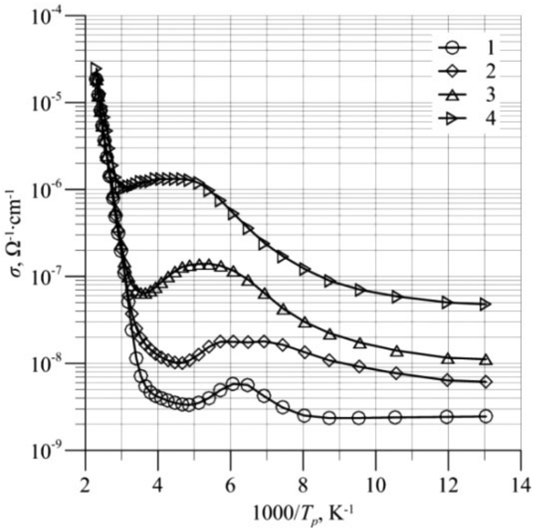

Fig. 2. Dependencies of $\sigma = f(1000/T_p)$ for n-type GaAs, poly-energy implanted with H^+ ions, for f: 1 – 1 kHz, 2 – 10 kHz, 3 – 100 kHz, 4 – 1 MHz. The annealing temperature is $T_a = 523$ K

The activation energy ΔE was determined for additional energy levels resulting from the implantation of H^+ ions. The method of determining the activation energy value is shown in

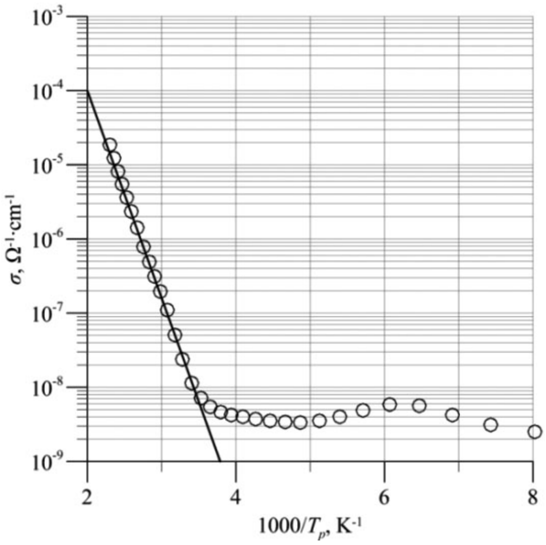

Fig. 3. Dependency graph of $\sigma = f(1000/T_p)$ for n-type GaAs, poly-energy irradiated with H^+ ions, annealed in temperature $T_a = 523$ K for the measuring frequency $f = 1$ kHz

Table 1. GaAs defective activation energies obtained for $f = 1$ kHz

Measurement frequency $f = 1$ kHz						
Annealing temperature T_a, K	**Range of measuring temperatures T_p, / Activation energy ΔE**					
	T_p, K	ΔE, eV	T_p, K	ΔE, eV	T_p, K	ΔE, eV
Without heating	113 ÷ 133	0.125	253 ÷ 283	0.610		
453	153 ÷ 193	0.078	273 ÷ 313	0.470	393 ÷ 433	0.600
473	153 ÷ 183	0.078	273 ÷ 313	0.470	393 ÷ 433	0.590
523	133 ÷ 173	0.054	293 ÷ 363	0.565	393 ÷ 433	0.625
573	123 ÷ 143	0.044	313 ÷ 403	0.565	413 ÷ 433	0.732
593					333 ÷ 433	0.679
643					383 ÷ 433	0.890
663					413 ÷ 433	0.840

Fig. 3 and the values read from it are $\sigma_0 = 10^{-9}$ $(\Omega\cdot\text{cm})^{-1}$ for $1000/T_0 = 3.75$ K^{-1} and $\sigma_1 = 1.34 \times 10^{-4}$ $(\Omega\cdot\text{cm})^{-1}$ for $1000/T_1 = 2.0$ K^{-1}. As a result, substituting these values into Equation (2) we obtain $\Delta E \approx 0.58$ eV.

4. Conclusions

As a result of the conducted research, based on the analysis of empirically determined Arrhenius curves, it was possible to identify a series of radiation defects with activation energies in the range (0.04 ÷ 0.84) eV, introducing additional energy levels in the bandpass GaAs sample subjected to poly-energy H^+ ion implantation. Their location was determined based on the energy of activation ΔE. However, in order to confirm whether the intermediate band was actually formed, it is necessary to perform further analyses. In particular, it is necessary to implement a new analytical model, which takes into consideration the phenomena associated with the thermally activated mechanisms of carrier transport as it was described in [16]. Moreover, the influence of specific parameters of ion implantation, post-implantation treatment and testing conditions should also be considered.

The results of the performed study could be analysed taking into account potential application in the photovoltaic industry, as it was concluded in [17], the intentional introduction of certain defects can be used to improve the efficiency of PV devices.

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