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The Influence of Nanofilled Polymer Coatings and Magnetic Field on the Decay Kinetics of Photovoltage in Silicon Crystals Used in Solar Energy

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The influence of a weak stationary magnetic field on the kinetics of photovoltage decay in "solar" silicon crystals (solar-Si) with nanofilled polymer coatings is studied. The characteristic features of magnetostimulated change of carrier lifetime depending on the concentration and the method of forming the nanofillers in the polymer matrix are established.

Keywords: Silicon, Magnetic field, Photovoltage, Structural defects.

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1. INTRODUCTION

In recent years, a number of experimental studies associated with the influence of a magnetic field on the state of the defect-impurity structure and properties of weak magnetic materials, which are characterized by the disordered magnetic structure (para- and diamagnetics) [1-6] has been performed.

However, a unique physical interpretation of the magnetic field influence on the real structure and structure-dependent properties of non-magnetic monocrystals has not yet been found. Gaps in the study of magnetostimulated changes of the structure and physical, in particular, electrophysical parameters of silicon, which is used in solar energy (solar-Si (s-Si) crystals), are especially noticeable. Therefore, investigation of these changes is reasonable, since they, firstly, reproduce the real conditions of functioning of solar cells (SC) frequently operating under the influence of magnetic fields, and, secondly, give quite specific information about the interaction of charge carriers (photocarriers), generated during absorption of electromagnetic radiation (photons), with structural inhomogeneities, whose appearance is conditioned by the magnetic action.

The mechanism of revealed changes was proposed by the authors of [7, 8] in the study of changes in the efficiency of silicon photoelectric transducers (PET) after magnetic treatment (MT) by a stationary magnetic field ($B = 0.2$ T, $t_{\mathrm{MT}} = 7$ days). According to this mechanism, MT induces a restructuring of the initial structure of point defects in the silicon master chip with the formation of metastable state of a new ensemble of complexes of point defects, which provides a lower concentration of recombination centers identified as deep recombination levels in the forbidden band of a semiconductor. As noted in [7, 8], decrease in the concentration of recombination centers conditions the observed after MT increase in the lifetime of non-equilibrium charge carriers and, as a consequence, induces the increase in the PET efficiency. Redistribution of recombination centers in Si crystals can be caused by not only certain treatments (chemical, radiation, magnetic), but also such processes as gettering and adsorption of impurities by the surface and also deposition of different coatings on the surface [9, 10]. At that, lifetime of carriers of the initial material can increase or decrease – both effects are observed. It is shown in the works [11, 12] that deposition on the surface of s-Si crystals of a polymer epoxy-urethane coating and long-term ($t_{\mathrm{MT}} = 200$ days) MT induce the increase in the lifetime of charge carriers and, thus, these factors can promote, in perspective, the increase in the SC efficiency.

Synthesis of nanofilled polymers is one of the methods for obtaining new materials with a unique complex of properties. Introduction of nanofillers into a polymer matrix allows to produce nanocomposites with an improved level of parameters inherent to polymers. An important problem is to ascertain the influence of nanofilled epoxy-urethane coatings obtained by different methods on the electrophysical characteristics of s-Si crystals.

The aim of this work consisted in the determination of changes in the decay kinetics of photovoltage in s-Si crystals with nanofilled (silicon-containing) epoxy-urethane coatings under the magnetic influence.

2. EXPERIMENTAL

Solar-Si crystals, doped with boron of resistivity of 5 Ohm·cm, with crystallographic orientation {100} were used in the work. Coatings of nanofilled epoxy-urethane polymers were deposited on the surface of s-Si samples. Synthesis of the inorganic filler was carried out by the sol-gel method by the hydrolysis-condensation reaction of tetraethoxysilane (TEOS) [13].

Formation of nanofilled epoxy-urethane polymers (nEU) was performed in two ways: I) synthesizing polysiloxane particles (PSP) directly in the medium of polyoxypropylene glycol (POPG); II) introducing into POPG the already formed sol and distributing it using ultrasonic dispersion. Based on the data of small-angle X-ray scattering, size of the obtained PSP was 5÷80 nm. Nanofilled polymer coatings formed by I and II methods are designated for brevity as nEU-1 and nEU-2, respectively.

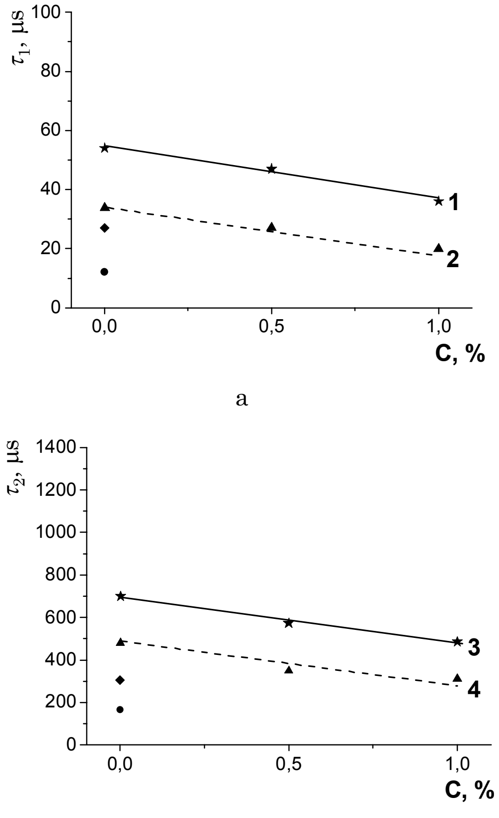
Investigations performed using IR-spectroscopy have showed that in method I (in situ) PSP, which are coupled with POPG by both hydrogen and covalent bonds, are formed in nPOPG. In method II formed PSP are uniformly distributed in POPG and coupled with it by hydrogen bonds only. Concentrations of the filler used in methods I and II in terms of mass % were equal to $C_1 = 0.001$ %, $C_2 = 0.5$ % and $C_3 = 1$ %. Thickness of the coatings obtained by methods I and II and deposited on the s-Si surface was 20 μm.

MT of the s-Si samples with polymer nanocomposite coatings consisted in the exposure of the studied samples in a weak stationary magnetic field with induction of $B = 0.17$ T during $t_{\mathrm{MO}} = 21$ days. Two decay components, namely the short-term (τ_1) and the long-term (τ_2), were determined by the kinetic dependences of the photovoltage decay. These components were defined before the beginning and immediately after the completion of MT. Photovoltage decay was measured using the condenser method [14]. Laser photodiode with wavelength of 650 nm was used for photovoltage excitation in s-Si crystals. Duration of pulses which excited the photovoltage was equal to 14 μs.

3. RESULTS AND DISCUSSION

Results presented in Fig. 1 indicate that deposition on the s-Si surface of the coatings of nanofilled epoxy-urethane polymers nEU-1 (obtained by the way I of the sol-gel method) at all concentrations of the filler leads to the increase in the short-term (τ_1) and long-term (τ_2) components of the photovoltage decay with respect to s-Si crystals without coatings and also with respect to s-Si crystals, on which a polymer coating without filler was deposited. At that, with increasing content of the filler introduced into a polymer matrix, the lifetime of carriers of τ_1 and τ_2 decrease.

In the case of deposition on the s-Si surface of nEU-2 coatings (dependences 2, 4 in Fig. 1), the effect associated with the increase in the carrier lifetime is less significant compared with s-Si crystals with nEU-1 coatings. It is not improbable that the observed in s-Si samples with nanocomposite coatings increase in the carrier lifetime on the surface, which is characterized by the parameter τ_1, and increase in the lifetime in the near-surface region, which correlates with the parameter τ_2, is conditioned by the passivating role of the coating. Indeed, if take into account that a large number of broken bonds acting as the recombination centers exists on the surface and in the near-surface region (in the vicinity of the s-Si/SiO_2 interface) of s-Si samples, then presence of the coating decreases the number of broken bonds and, correspondingly, induces the increase in the carrier lifetime. In explaining the mechanisms underlying the revealed effects, one should pay attention to another circumstance. The structure, in which, in contrast to the method I, chemical interaction between the filler (PSP) and epoxy-urethane is absent, is formed in the method II of formation of nanocomposite coatings [13, 15]. In this connection, it can be assumed that presence of only physical interaction of PSP with an organic matrix decreases the passivaiting function of the coating. In our view, it is possible that the degree of passivation is also determined by the adhesion strength of filled epoxy-urethanes (nEU). Approximating the results of investigation presented in [15] to our experimental results, the following assumptions can be made. Higher adhesion strength of nEU-1 compared with nEU-2 leads to the fact that their passivating function is expressed more significantly. The latter conditions higher values of the lifetime of carriers in s-Si crystals in the presence on their surface of nEU-1 coatings compared with the lifetime in s-Si crystals in the presence on their surface of nEU-2 coatings. Decrease in the carrier lifetime with increasing content of the filler in nEU-1 from 0.001 % to 1 % correlates well with the established in [15] decrease in the adhesion strength of the coatings at PSP concentration of 1 %.



b

Fig. 1 – Dependence of the short-term (a) and long-term (b) components of the photovoltage decay in s-Si crystals with nanocomposite epoxy-urethane nEU-1 (1, 3) and nEU-2 (2, 4) coatings on the concentration of the silicon-containing filler. s-Si samples: ● – without coatings; ◆ – with EU coating without filler

Our study revealed the differences in the behavior of the carrier lifetime in s-Si crystals with nanocomposite nEU-1 coatings, which underwent MT, and in s-Si crystals with nEU-1 coatings which were not magnetically treated (see Fig. 2).

At that, as seen from Fig. 2, the value and sign of the effect conditioned by the magnetic field action, depends on the concentration of the silicon-containing filler. At small PSP concentration (0.001 %), effect associated with the MT influence is absent. Increase in the PSP concentration to 0.5 % induces the increase in the carrier lifetime τ_1 and τ_2 after MT. At the same time, decrease in the carrier lifetime is observed at the filler concentration of 1 % after MT.

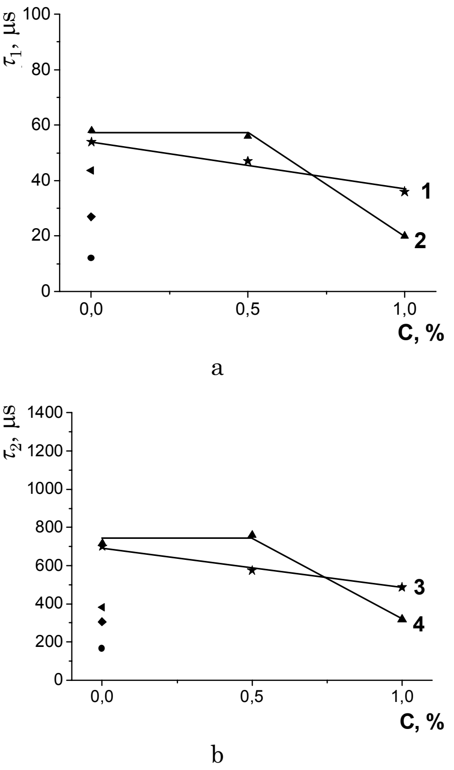


Fig. 2 – Dependence of the short-term (a) and long-term (b) components of the photovoltage decay in check s-Si samples with nEU-1 coating (1, 3) and in s-Si samples with nEU-1 coating after MT (2, 4) on the concentration of the silicon-containing filler. s-Si samples: ● – without coatings and not magnetically treated; ◆ – with EU coating, without filler and not magnetically treated; ◀ – with EU coating, without filler and after MT

Analysis of the dependences of magneto-stimulated change in s-Si crystals with nanocomposite nEU-1 and nEU-2 coatings illustrated in Fig. 3 leads to the following conclusion. Magneto-stimulated change effects of the lifetime for the PSP concentration of 1 % in the case of nEU-1 and nEU-2 coatings are opposite in sign.

At filler concentrations of $C \leq 0.5$ %, carrier lifetime increasing effect induced by the magnetic action in s-Si crystals with nEU-1 coating is more significant in comparison with the effect observed in s-Si crystals with nEU-2 coating. At the same time, at filler concentrations of $C = 1$ %, carrier lifetimes in s-Si crystals with nEU-1 coating after MT have lower values compared with the case associated with deposition of nEU-2 coating. The obtained results allow to assume that at filler concentration of $C \leq 0.5$ %, concentration of recombination centers in s-Si crystals with nEU-1 coatings after MT is lower than in s-Si samples with nEU-2 coatings. At filler concentration of $C > 0.5$ %, magneto-stimulated effect of the carrier lifetime change becomes opposite in sign. This sign inversion of the discovered effect depending on the filler concentration and way of its formation can be associated with both the structural features of synthesized nEU-1 and nEU-2 nanocoatings and with their charge state. Investigations performed using the IR spectroscopy method [13, 15] allowed to reveal that PSP included into the epoxy-urethane matrix contain both Si-O-Si groups and SiOH silanol groups. As it is noted in [16], SiOH group can act as an electron trap. It is not improbable that magneto-stimulated changes of the decay kinetics of the photovoltage can be associated with the electrophysical processes occurring at the polymer matrix/filler interface. It can be assumed that with increasing amount of the filler to 1 % in nEU-1 coating, effective surface of the interface increases and additional carrier trapping centers are formed, and this, in turn, leads to the decrease in the carrier lifetime.

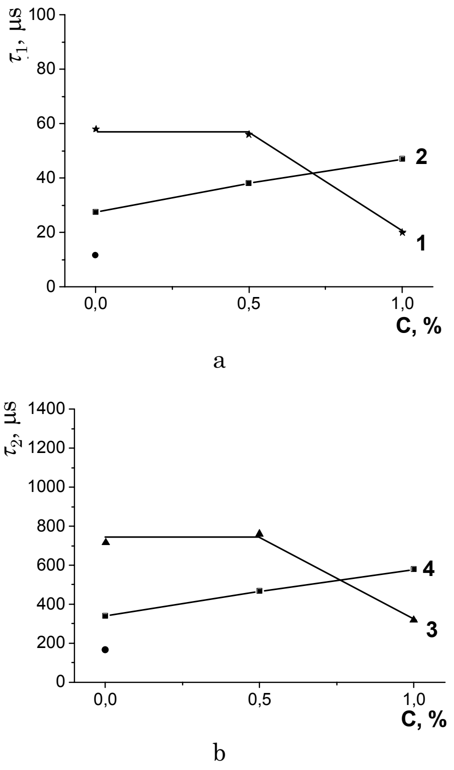


Fig. 3 – Dependence of the short-term (a) and long-term (b) components of the photovoltage decay in subjected to MT s-Si samples with nEU-1 coating (1, 3) and s-Si samples with nEU-2 coating (2, 4) on the concentration of the silicon-containing filler. s-Si samples: ● – without coatings and not magnetically treated

At certain values of the filler concentration ($C = 1$ %) in nEU-2 coating its particles form agglomerates, and, probably, in this case integral surface of the interface decreases. It is not improbable that a number of traps at the interface decreases, and, correspondingly, carrier lifetime increases (see dependences 2, 4 in Fig. 3).

The obtained results allow to conclude that magneto-stimulated changes of the decay kinetics of the photovoltage and, consequently, changes in the carrier lifetime depend on both the way of formation of a nanocomposite coating deposited on the s-Si surface and the filler concentration in the coating. These results should be taken into account in the development of recommendations concerning the possibility of the SC efficiency enhancement due to the influence of two factors: the 1-st factor is associated with deposition on the s-Si surface of nanocomposite epoxy-urethane coatings with the filler; the 2-nd influence factor consists in MT of s-Si samples with nEU in a weak ($B = 0.17$ T) stationary magnetic field.

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