

Semiconductor surface spectroscopy using transverse acousto-electric effect: Role of surface charge in photo-processes at the ZnS/Si interfaceN.P. Tatyanyenko¹, N.N. Roshchina¹, V.L. Gromashevskii¹, G.S. Svechnikov², L.V. Zavyalova^{1*}, B.A. Snopok^{1**}¹*V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41, prospect Nauky, 03680 Kyiv, Ukraine***E-mail: zavjalov007@gmail.com;**** E-mail: snopok@isp.kiev.ua*²*National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute" 37, prospect Peremohy, 03056 Kyiv, Ukraine*

Abstract. The effect of illumination in the visible spectral range on the magnitude of transverse acoustoelectric effect (TAE) in ZnS/Si structures was studied using a noncontact surface acoustic wave device based on the acoustoelectronic structure with an air gap. ZnS films were obtained using pyrolysis of the chelate organometallic complex, zinc diethyldithiocarbamate, on Si substrates within the temperature range 220 to 260 °C. It has been established that the charge of the adsorption origin on the external surface of the ZnS film strongly influences the photo-processes in the structure under consideration. For the samples with a small surface charge, the value of TAE decreases rapidly with the increase in illumination power due to an increase in the concentration of non-equilibrium carriers. For the samples with a large surface charge, the barrier-trap mechanism of photogeneration is observed, in which the appearance of non-equilibrium carriers is accompanied by their capture and subsequent thermalization. This compensating mechanism explains well both stabilization of the magnitude of TAE by a distributed system of traps with rather large capacitance, and the specific shape of dependence of the TAE magnitude on illumination power. The technique developed by us on the basis of the transverse acoustoelectric effect in the layered piezodielectric / air-gap / semiconductor structure is a powerful tool for non-contact determination of the charge state of film structures, depending on their deposition parameters and various external conditions.

Keywords: transverse acoustoelectric effect, ZnS/Si structure, photo-processes, surface charge.

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1. Introduction

$A^{II}B^{VI}$ semiconductors have already conquered the honored place among the materials for the elements and systems for optoelectronics applications [1]. From a retrospective view, zinc sulphide has been the most widely used for industrial luminophors [2]. ZnS single crystals, for which the ionic bonds are the strongest among those of $A^{II}B^{VI}$ compounds, are characterized by low electron and, especially, hole mobility; piezoelectric properties (the non-centrosymmetrical face-centered lattice type with the high coefficient of electromechanic bonds), large hardness, the wide band gap (transparent in the visible spectral range) and relatively low density [3].

Despite its more than half a century history as an industrial material, zinc sulphide did not lose its significance for scientific researches, but, rather, it has substantially increased it. This is caused by the increasing use of this material for production of unique nanoscale structures, especially for the solar energy and water decomposition applications [4-6].

In accordance with this, the features of the surface states of ZnS come to the forefront of scientific researches, since the contribution of surface atoms to the bulk of material increases with the decrease in the size of the structure [7].

Among the variety of scientific problems related to the functional properties of ZnS nanostructures, one of

the most important problem is the necessity to control their surface charge, since this property is the main one for ensuring the stability of nanobots: the ability to control the surface charge enables to avoid aggregation of nanoparticles and, thus, develop appropriate technological ways for their deposition and modification, etc.

Despite the fact that existing modern methods of studying nanostructures make it possible to obtain the characteristics of individual nanoparticles (for example, DSL, etc.) when analyzing their surface charge certain difficulties arise, which are related to the contribution of their surrounding medium. Therefore, to analyze the surface properties of ZnS due to the peculiarity of its preparation and the type of precursors used, thin films were obtained using organic zinc salts pyrolysis in the gas phase above the surface of the heated substrate. It should be emphasized that the previously proposed [8, 9] precursors based on diethyldithiocarbamates now find an ever wider application for obtaining nanostructures [10, 11].

The composition of zinc oxide and zinc sulphide films obtained by sputtering on a heated substrate of zinc diethyldithiocarbamate (DDC-Zn) at the atmospheric pressure depends on the degree of precursor purification, the substrate temperature (with an increase from ZnS up to ZnO), the deposition rate (with an increase from ZnO to ZnS) and annealing at 600 °C (transform into ZnO) [12]. In ZnS films with the most perfect crystal structure, obtained from a precursor with the maximum degree of purification, the intense edge luminescence (3.64 eV) was first observed at room temperature. Two-phase ZnS-ZnO films obtained from an inexpensive precursor are characterized by strong piezoelectric properties and can be used to develop piezoelectric and acoustoelectronic devices.

The purpose of this paper is to investigate the peculiarity of the surface charge of the ZnS films fabricated in the technological conditions by using contactless acoustoelectric techniques under illumination in the visible region.

2. Objects of research and experimental methods

Zinc oxide and zinc sulphide films were obtained by sputtering onto a heated substrate (Si wafer, thickness 0.35 mm) of DDC-Zn in the air at the atmospheric pressure similarly to Refs. [13, 14]. In the course of the experiment, the precursors rate of sputtering and the temperature of the substrate were varied, and also starting materials of different purity were used.

As a starting material (precursor) DDC-Zn was used in one of three types: DDC-Zn, which is manufactured under the trademark type (type I), DDC-Zn, synthesized using the laboratory method from DDC-Na and ZnCl₂ reagents (type II), DDC-Zn, obtained from reagents of the grade "hch", further purified before synthesis by using the method of extraction of chelates (type III) [15, 16]. As a result of purification, the content of metal

impurities (nickel, palladium, platinum, traces of copper and cobalt, iron and copper hydroxides) decreased from 3·10⁻² (type I) down to 8·10⁻³ wt.% (type II) and to 2·10⁻³ wt.% (type III).

The films were prepared by spraying a 0.1 M solution of DDC-Zn in pyridine onto a heated up to 220–260 °C Si wafer placed on the high temperature C-48 glass plate, with the solution sputtering rate within the range 0.8...2.0 ml/min.

It should be noted that the indicated temperature corresponds to the substrate temperature throughout the sputtering process, while before sputtering it exceeds the above specified one by 80...100 °C, but when sputtering the solution at the rate close to 1 ml/min the temperature decreases to a predetermined value in 30...40 s.

To study the surface structures of ZnS, we developed an approach that allows noncontact monitoring of the surface charge using a transverse

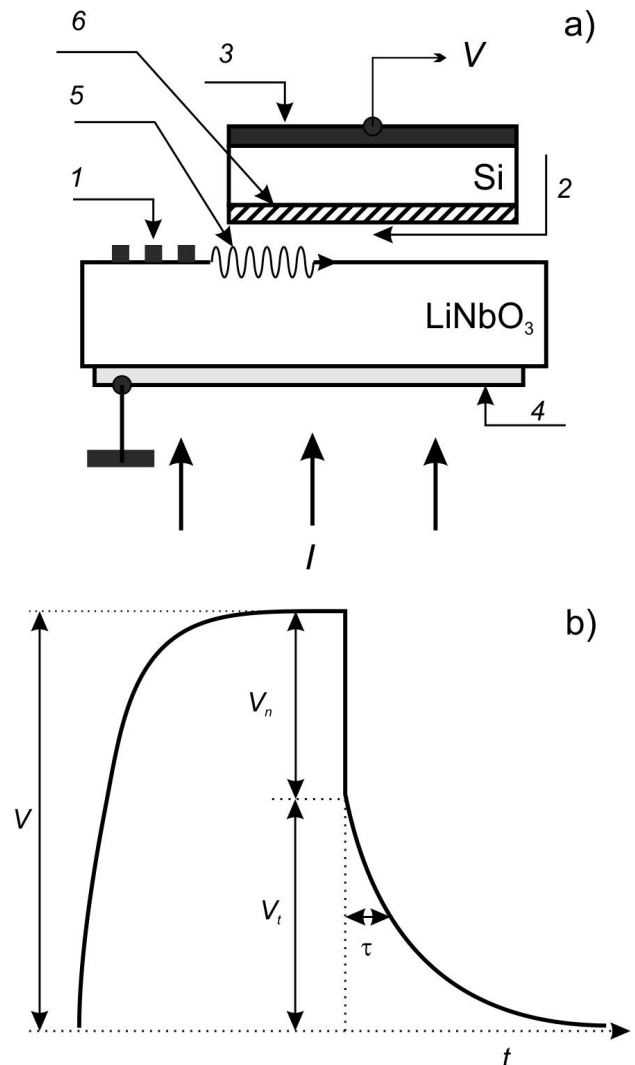


Fig. 1. The AEPSAG scheme (a) and the signal parameters of TAE (b). *I* – an input interdigitated transducer (IDT), 2 – air gap, 3 – metal electrode, 4 – SnO₂ semitransparent electrode, 5 – SAW pulse, 6 – ZnS film. *V*, *V_t*, *V_n* are the amplitudes of TAE, trap and concentration components of TAE, respectively; τ is the half-life time of the trapped component of TAE; *I* – illumination with a RGB type LED.

acoustoelectric effect (TAE) [17, 18]. The electromagnetic field of the surface acoustic wave (SAW) penetrating into the semiconductor region propagating in the piezoelectric substrate (Fig. 1) causes a displacement of the free charge carriers, inducing the corresponding in-phase changes in the potential on the surface of the semiconductor.

The analysis of the features of the manifestation of the field effect on TAE in a semiconductor made it possible to develop a method for monitoring the charge state on a surface; a detailed description of the methodology can be found in [19-21]. In other words, the change in the surface charge leads, through the field effect, to a change in the resistivity of the near-surface region of the space charge of semiconductor, and, accordingly, to the magnitude of TAE. As a result, small changes in the value of charge localized in the surface structure are transformed into a near-surface conductivity of semiconductor, which is easily measured by the contactless method. The nature of the surface charge can be very different, from the conditioned procedure to the adsorption or photoinduced, *etc.*

To measure TAE (Fig. 1), we used yZ -LiNbO₃, in the z direction of which SAW was excited at the frequency of 37 MHz, duration close to 1.0 ms, the repetition rate of 10 Hz, and the counter-transducer of aperture 1.8 mm. The gap (0.2 μ m) between the semiconductor and piezoelectric in the acoustoelectronic piezoelectric-semiconductor structure with the air gap (AEPSAG) was provided by a system of supports on LiNbO₃. The supports were created by etching the piezoelectric with an ion beam [22].

An RF signal applied to AEPSAG will generate SAW, a signal of TAE was registered across the Si-LiNbO₃ structure. The shape and parameters of this TAE signal are shown in Fig. 1.

As substrates, low-resistance Si p -type plates were used, on which ZnS films were deposited. From the obtained structure 5x2x0.35 mm samples were cut off and installed in AEPSAG. All the manipulations with the samples were carried out under ambient air conditions.

Illumination of the structure was carried out using an RGB type LED at three wavelengths: 475, 525 and 635 nm through a semitransparent SnO₂ electrode that was deposited on the back side of LiNbO₃. The LED power was calibrated at these three wavelengths by using the Hamamatsu S2386-44K photodiode.

3. Transverse acoustoelectric effect in ZnS/Si structures

Table 1 and Fig. 2 show the results of TAE investigation in ZnS/Si structures in the dark in the air atmosphere (Fig. 1). It was found that all the samples are characterized by the negative sign of the TAE value. This means that the high-resistivity (in comparison with that of bulk) surface region formed at the Si-ZnS interface have the p -type conductivity. The analysis of the dependence of the maximum value of TAE (in a series of 5–10 samples of each type) on the substrate temperature is shown in Fig. 2.

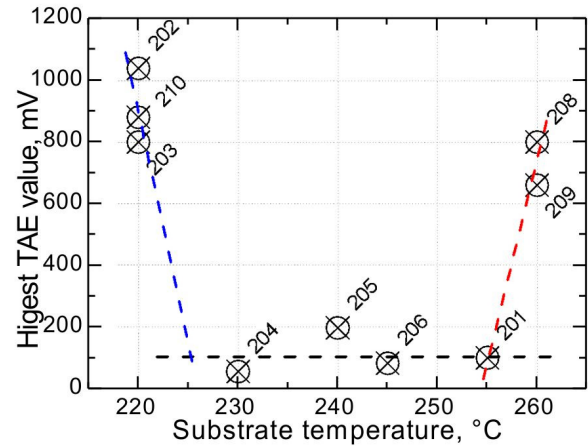


Fig. 2. Dependence of the maximum value of acousto-emf on the substrate temperature during deposition (201–210 – numbers of the samples).

Table 1. The main characteristics of the thin-film ZnS/Si structures and the maximum value of TAE observed under conditions without illumination. The numbers indicated in the table correspond conditionally to the samples obtained in different technological regimes.

Sample No.	Precursor type	Cu content, wt. %	Substrate T , °C	Film thickness, nm	Growth rate, nm/min	V_{max} in the dark, mV	τ , ms
201	I	–	250	500	50	–98	0.35
202	I	–	220	500	29	–1040	0.8
203	III	0.2	220	650	46	–800	0.6
204	II	–	230	350	16	–53	0.45
205	III	–	240	500	28	–195	0.4
206	I	0.2	240	650	33	–65	0.45
207	I	–	240	420	28	–29	0.3
208	III	–	260	350	50	–800	0.8
209	I	0.2	250	350	35	–660	0.9
210	III	0.2	220	650	36	–880	0.7

As it follows from Table 1 and Fig. 2, the value of TAE V depends most strongly on the substrate temperature (Fig. 2). The highest values of V were obtained at low substrate temperature (220 °C). Comparable values were also observed with an increase in temperature up to 260 °C.

Since the temperature of substrate has a significant effect both on the phase composition of the films and on the number and type of defects, it is probably these reasons that cause formation of charged states in ZnS films. At low temperatures (less than 220 °C), structural defects are the main ones, whereas at high temperatures (higher than 260 °C) – the mismatch of the energy levels of the band structure in the contact areas of the ZnS main phase and the emerging ZnO nanoclusters.

The analysis of relaxation time inherent to the trapped component of TAE confirms this conclusion – large TAE values are also characterized by longer relaxation times. At the same time, it should be noted that it is not possible to attribute the effect of charging the surface to the ZnO states, a sample containing exclusively ZnO (sample No. 207, precursor-zinc acetylacetonate) [22] did not demonstrate any significant TAE response.

As it was shown, the chemical purity of reagents does not significantly influence the value of TAE. This can be explained by the fact that the impurities present in reagents (also in the form of diethyldithiocarbamates, rather than salts) probably do not take part in formation of these films, since their amount is negligible, and they are displaced by the decomposition products of the main precursor, zinc diethyldithiocarbamate.

The univocal effect of the sputtering rate (within the range 0.8 to 2.0 ml/min) on the TAE value was not established; some influence may occur, at least as a result of stronger cooling of the substrate as the intensity of the supply of reagents increases. As shown by the growth kinetics of such films [23], in the range of low precursor concentrations (0.1 M) used in this work, the quality of crystallites, their structural perfection at this low vapor pressure of the precursor are practically independent of the speed of its dispersion and, consequently, the growth rate of the film. This is caused by the fact that the film-forming elements under these conditions can be embedded into the sites of crystal lattice, and the by-products of decomposition manage to leave the synthesis zone due to the high temperature and flow of gaseous components.

It is interesting to note that irrespective of the type of precursor, the presence of copper, rate of supply of reagents and difference in their volumes by no more than 10...15% (Table 1), the thickness of the films synthesized at high temperatures is almost half of that obtained at temperature of 220 °C. This clearly indicates a change in the film growth mechanism in such a narrow temperature range.

4. Peculiarities of charge formation and localization in ZnS films

The surface acoustic-emf method does not directly indicate the position/location of the charge in the samples. For example, since formation of a transition layer in silicon with an excess of sulfur can occur at the beginning of the film formation process, which can lead to a change in TAE. To evaluate location of the charge, step-by-step etching of the film was carried out. First, we investigated the effect of gradual, stepwise long etching of samples on the value of TAE. Etching was carried out in a weak solution of hydrochloric acid (0.2%) until the film was completely etched out (11 min of etching corresponds to a complete removing the 0.5- μ m film in the sample 202). The change in the value of TAE in the samples ZnS/Si as a function of their etching time is shown in Fig. 3.

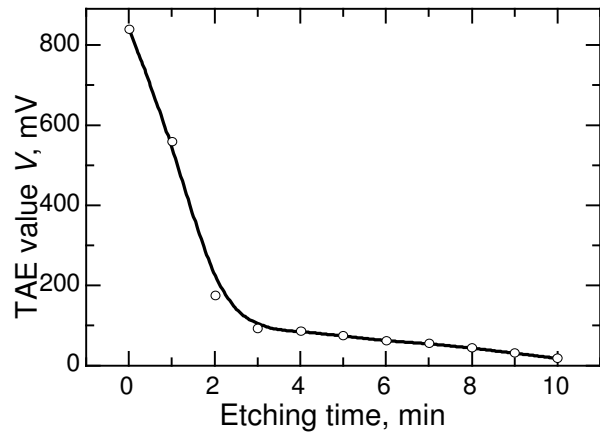


Fig. 3. Dependence of the transverse acousto-emf on the etching time of the sample (No. 202). Etching was carried out in a weak solution of hydrochloric acid (0.2 vol.%) until the film was completely etched out.

Possible doping the near-surface layer of silicon by the sulfur impurity during deposition of films does not occur. The signal of film almost completely etched corresponds to the signal of silicon sample without a film. This is probably caused by the low substrate temperature and a short exposure time, which is not sufficient for confident doping the semiconductor material [24-26]. Moreover, taking into account the peculiarities of temperature decomposition of metal dithiocarbamates, under these conditions, Zn-S bonds do not break, and free sulfur is contained in the reaction space in a small amount [27-29].

Thus, it can be assumed that the observed values of TAE are related to the presence of a positive charge distributed in the ZnS film in the immediate vicinity of the silicon surface. This charge can be both of the biographical origin, and induced in the bulk by the surface states of the opposite sign. The latter, as it is well known, is associated with the oxygen centers of adsorption origin, the negative charge of which is related with the capture of electrons from the near-surface region of the material [30-32].

This model is in good agreement with the results of layer-by-layer etching the ZnS films in a weak water solution of hydrochloric acid (0.2 w.%). As it follows from Fig. 3, the greatest influence on the value of TAE is caused by etching at the initial section, – a sharp drop in the value of TAE is observed in the first 2 min of etching, when the thickness of the film decreases by approximately 15%. This testifies to the fact that the primary cause of high values of TAE is the surface charge of adsorption origin localized on the outer surface of the ZnS film.

5. Peculiarities of TAE under illumination

The magnitude of the acousto-emf depends on the concentration and mobility of free carriers, charge on the surface states, the amplitude of induction induced by SAW on the surface of semiconductor and the initial bending of bands [19, 20, 22]. Since illumination in the

absorption region can substantially change a number of these characteristics, the use of light is a powerful tool for studying the surface of semiconductors. In the case of ZnS/Si structures, in the visible spectrum only semiconductor can absorb light, and the coating, if present on its surface, is optically transparent.

When photons, which energy is higher than the forbidden gap (about 1.11 eV (~1117 nm) for silicon) are absorbed, electron-hole pairs are generated in the semiconductor the fate of which depends on the characteristics of the space charge region (SCR) near the surface. First of all, the bulk Dember photo-emf is formed, due to the inhomogeneous spatial distribution of the light-generated carriers and the difference in the mobility of charges of different signs; practically for all semiconductors electrons have higher mobility than holes, and they diffuse more rapidly into the non-illuminated region [33]. However, in the present case Dember emf contribution can be ignored, since its value does not depend on the charge states on the surface, and accordingly, has approximately the same value in all the samples.

The penetration depth of light into silicon is approximately $6.25 \cdot 10^{-5}$ cm (absorption coefficient $1.6 \cdot 10^4$ cm $^{-1}$), $1.2 \cdot 10^{-4}$ cm ($8.325 \cdot 10^3$ cm $^{-1}$), $3.2 \cdot 10^{-4}$ cm ($3.155 \cdot 10^3$ cm $^{-1}$) for 475, 525 and 635 nm, respectively, whereas depletion width is typically about a few micrometers for silicon, and it decreases as the dopant concentration goes up. Thus, for the spectrum considered by us, absorption occurs predominantly in SCR, and the carriers of different signs generated by the light are spatially separated under the action of the surface-barrier field. The result of this change in SCR results in partial compensation of the original field in the near-surface region and is expressed in a corresponding decrease in the magnitude of the band bending.

If the only process under photoexcitation is an increase in the number of charge carriers, the dependence

Table 2. The value of TAE in the ZnS/Si structures under illumination with a light-emitting diode at three wavelengths for the backlight power ~23 μ W.

Sample No.	V_0 in the dark, mV	$\Delta V/V_0$, % under illumination $\lambda = 475$ nm	$\Delta V/V_0$, % under illumination $\lambda = 525$ nm	$\Delta V/V_0$, % under illumination $\lambda = 635$ nm
201	-52	-92.3	-96.2	-96.2
202	-840	-28.1	-36	-41.6
203	-420	-54.7	-60.5	-64
204	-20	-92.5	-96.2	-95.1
205	-128	-66.7	-74.2	-84.1
206	-65	-80	-89.2	-87.7
208	-690	-4.1	-11	-19.9
209	-480	-91	-95.4	-96.2
210	-700	10	2.9	-5.7

of the photo-emf on the intensity (in the region of small values) is monotonic function [34]. When the illumination intensity is increased, full compensation of the surface curvature of the bands usually occurs, the bands are straightened, TAE tends to zero, and the photo-emf is equal to the dark bending of the bands on the surface of semiconductor.

The analysis of results obtained for the influence of ZnS/Si structures illumination at three wavelengths: $\lambda = 475, 525$ and 635 nm within the framework of the approach considered above allowed us to establish the following regularities. At a minimum illumination power (for all the wavelengths c.a. 23μ W), it was found that for a large number of samples (the TAE values of which without illumination are small), there is a sharp drop in the value of V under the influence of illumination (Fig. 4), the relative changes in $\frac{V - V_0}{V_0} = \frac{\Delta V}{V_0}$ are

negative and constitute from 50 to 100% of the dark response (Table 2). The nature of the decay of TAE of the illumination power is the same for different samples and is well described by the function of a stretched exponent specific for the environments with nano-micro-dimensional topological non-ordering [35, 36]:

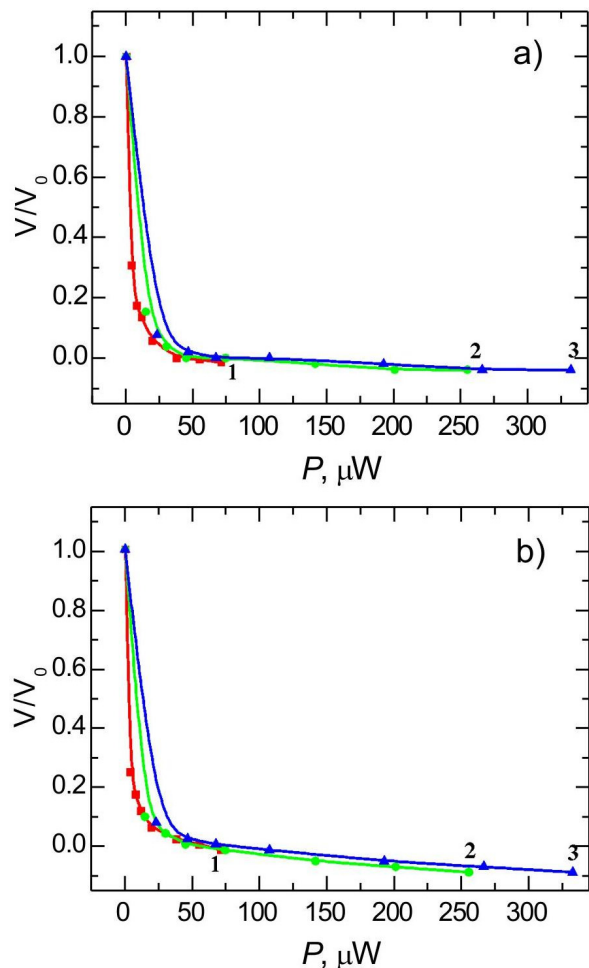


Fig. 4. Dependences of the normalized value of TAE on the illumination power for the samples Nos. 201 (a) and 204 (b). λ : 1 – 635 nm, 2 – 525 nm, 3 – 475 nm.

$$V/V_0(P) = \exp\left[-\left(\frac{P}{P_0}\right)^\beta\right], \quad (1)$$

where $V/V_0(P)$ is the relative value of TAE, $0 < \beta < 2$ and P_0 – parameter that has the power dimension. In general, one can say that at the phenomenological level, non-exponential relaxation of the form (1) is the general form of evolution of surface type complex systems, and λ is a marker of a certain process, which allows it to be distinguished from a series of similar ones.

Analysis of the features of manifestation of non-exponential dependences for the TAE value on the illumination power (Fig. 4) makes it possible to conclude that in most cases (No. 201, 204, 206) the β value does not exceed 0.5 ± 0.1 and decreases with increasing the quantum energy (λ decreases). Moreover, the characteristic value of the decay P_0 also decreases to some extent. It indicates that for the samples with small values of dark TAE, a large variety of heterogeneous processes leads to a decrease in TAE under illumination, the activation of which occurs already at sufficiently low illumination powers.

For example, for the samples under consideration, even at the minimum illumination power, the value of $\Delta V/V_0$ varies within the range from -54% to -92% for $\lambda = 475$ nm; within the range from -80% to -96% for $\lambda = 525$ nm; and within the range from -64% to -95% for $\lambda = 635$ nm. Despite the fact that there is a fairly wide variation in the value of $\Delta V/V_0$ from the sample to the sample that could not be directly related to the technological parameters, the samples with the lowest V_0 values (No. 201, 204, 206) have a decrease $\Delta V/V_0$ within the range from -80% down to -92% .

Comparing the values of $\Delta V/V_0$ obtained for various wavelengths, we can state that with decrease in λ , the process of TAE decrease accelerates, that is, at $\lambda = 475$ nm it occurs faster than at $\lambda = 635$ nm. This is probably caused by the fact that the absorption coefficient of silicon grows with the decrease of wavelength, and the carriers generated by light are closer to the surface of semiconductor, where the field separating them has the maximum value.

As a result of similar studies at higher values of the radiation power of LED with the same values of λ (approximately 45, 68 and 88 μW), a number of dependences have been established. It should be noted that for the samples with a minimum value of TAE in the dark, illumination at the minimum used radiation power resulted in a complete compensation of TAE and, accordingly, in its zero values.

In contrast to the said above, the samples with high dark V_0 values (Nos 202, 203, 208, 210) are much less responsive to illumination and retain fairly high values of TAE even at the maximum illumination power (Table 2).

In this case, the spectral dependence of the effect correlates with the change in the absorption coefficient of silicon in this spectral region (Fig. 5). It can be seen from Fig. 6 that with increasing the illumination power, the value of $\Delta V/V_0$ continues to increase, reducing the value

of V for the majority of samples. And at the maximum (in our experiments) illumination power of 250...330 μW , the transverse acousto-emf value for this sample remains very significant: typically 220...245 mV and the sample No. 210 has more than 80% of the maximum V value in the dark (880 mV). Moreover, for the sample No. 210, in contrast to all other samples, when illuminating with a short-wave LED, there is no decrease in V , but a slight increase (up to 10%), which changes to a small decrease (down to -5.7%) with an increase in λ up to 635 nm. This behavior does not fit into the above model of surface processes and requires the involvement of additional mechanisms.

According to the classical model, which describes well the processes in samples with a weak manifestation of TAE in the dark, the signal of TAE decreased due to an increase in the carrier concentration with increasing the light power, since traps in the interface region unable to compensate sharp increase in free non-equilibrium

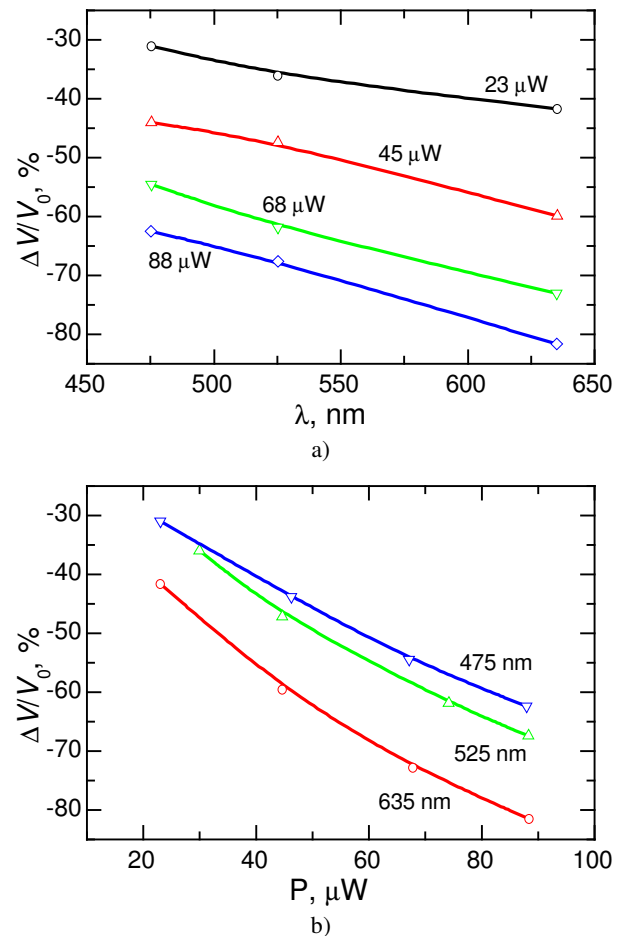


Fig. 5. Dependences of $\Delta V/V_0$ on the backlight wavelength for different backlight power (a) and on the backlight power for different wavelengths (b) for the sample No 202. The size of symbol illustrates the measurement error.

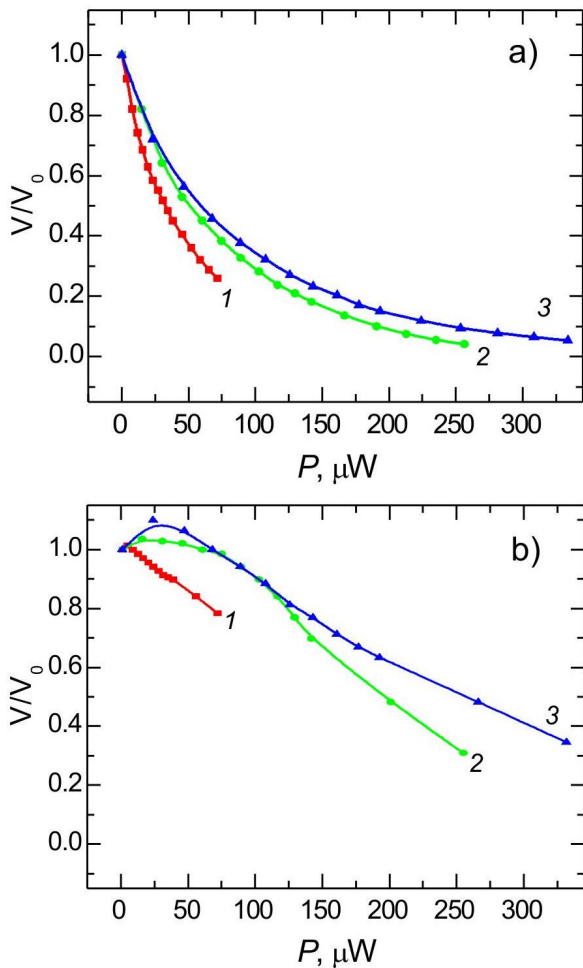


Fig. 6. Dependences of the normalized value of TAE on the illumination power for the samples Nos. 202 (a) and 210 (b). λ : 1 – 635 nm, 2 – 525 nm, 3 – 475 nm.

carriers; the conductivity of the near-surface layer increased, and the value of TAE decreased. This situation occurs, if the initial bending of the bands is small, the number of traps is small, and they are “fast” (the decrease in the trap component of the acousto-emf is characterized by small values of τ , see Table 1). In this case, the dependence of the signal from TAE on the intensity of light is due to the efficiency of barrier photo-emf generation, which compensates the initial bending of the bands and reduces TAE. It was found that such dependence is observed also after etching out the main part of the samples with a large dark value of TAE, as well as for whole films with an initially low TAE signal in the dark.

However, in the structure under consideration, in parallel with the barrier photo-emf, another mechanism can also be realized, which is associated with the preferential capture of non-equilibrium carriers of the same sign at the surface states and, consequently, with a change in the charge distribution within SCR under illumination. Since the effect of separation of non-equilibrium carriers described above by the SCR field with subsequent partial compensation of the initial

bending of the bands also takes place, this mechanism is usually called as the barrier-trapping one.

Indeed, if in the region of generation of non-equilibrium carriers there is a wide spectrum of “slow” traps (probably at the interface Si/SiO_x) with a very different capture cross section for electrons and holes, the character of the dependence varies substantially and has the shape similar to that shown in Fig. 6b (theoretical justification of these regularities can be found in [34]). The “stabilization” effect is more pronounced for blue light, since the depth of its penetration in Si is smaller, and the non-equilibrium carriers are localized predominantly near the surface, where most of the capture levels are located. For most of the samples with the dependence shown in Fig. 6a (202, 209, etc.), $V/V_0(P)$ is well described by the function of the stretched exponential with the values $\beta > 0.5 \pm 0.1$; the value of β increases with increasing the wavelength. This indicates that the variety of processes leading to a fall in the value of TAE under illumination decreases: some mechanism, for example, trapping, is increasingly prevalent in the system and levels out the contribution of other processes to the net effect. It should be noted that “slow” trap states at the interface are also manifested in the kinetics of TAE without illumination, where a long “tail” of the trap relaxation component (τ) typical for such processes is observed (see Table 1).

Special attention should be paid to the possible “nature” of these slow traps. Indeed, as it was shown above, the main “actors” are concentrated at the outer surface of ZnS (adsorption induced surface charge), whereas the non-equilibrium carriers are generated in the near-surface region of silicon. Thus, we can state that the charged centers on the outer surface of ZnS in some way influence redistribution of non-equilibrium carriers in silicon. Moreover, this process depends a little on the illumination power and can even lead to an increase in the acoustic-emf signal (see Fig. 6, curve 3). Indeed, for small illumination levels, the signal of TAE even slightly increases (No. 210), which is probably due to the approximation of the carrier concentration in SCR to the values optimal for the generation of TAE (since the conditions for generating the maximum signal of TAE are defined by two mutually opposite trends – the near-surface layer resistance and the free carrier concentration in it, see, for example, [19, 20, 22]).

The most likely explanation for the dependences shown in Fig. 6 is the mutually consistent behavior of the negative surface charge (adsorbed centers of oxygen) at the ZnS-atmosphere interface, the corresponding positive charge inside the ZnS film and the space charge region in silicon. If the signal of TAE is low, there is no surface charge on ZnS, the processes in silicon proceed in SCR without any influence from the coating. If, however, the charge on the ZnS surface is large enough to influence the bending of the bands on the silicon surface by means of a positive charge in the bulk of the ZnS film, the appearance of photocarriers leads to a complex sequence

of self-consistent processes that involve the capture and release of non-equilibrium carriers of different signs. Such a “compensating” mechanism that “stabilizes” the signal of TAE (band bending) by a distributed system of traps with a sufficiently large capacitance can well explain both the weak dependence of TAE on the illumination power and the special shape of this dependence. The most interesting features of this system of traps are its rather high capacity, since in some cases (No. 210) it allows stabilizing the value of TAE at relatively high illumination powers, and the ability to “self-activation” only at sufficiently large values of the surface charge.

6. Conclusion

The method of acoustoelectronic spectroscopy based on TAE has been successfully applied to study the features of the surface charging of the ZnS films and the effect of this charge on the photoprocesses in the ZnS film – a low-resistance Si substrate structure. When investigating the value of TAE in the dark, it was ascertained that the high-resistivity regions formed at the Si-ZnS interface have the *p*-type conductivity. The effect of film deposition conditions on the characteristics of the ZnS/Si interface was not revealed.

As a result of investigation of TAE in the ZnS/Si structures obtained under different conditions, dependences of the amplitude of TAE V on the process parameters have been determined. It has been established that the dark values of the amplitude (V_0) vary over a wide range (more than 20 times). The highest values of V_0 were obtained at low substrate temperatures (220 °C) and small film thickness (0.35 μm). When investigating the layer-by-layer charge distribution in the film, it was found that the main part of the charge responsible for formation of TAE is localized on the surface and in the near-surface region of the film.

Investigation of TAE under illumination at $\lambda = 475, 525$ and 635 nm at various illumination powers from 23 up to $330 \mu\text{W}$ showed that under the influence of illumination with increasing in λ , a decrease in the V value is observed, and it increases with increasing the illumination power. For the samples with a small surface charge, the dependence of V on the illumination power is well described by the function of the stretched exponential and is due to the barrier mechanism for generation of non-equilibrium charge carriers. For the samples with a large value of V_0 , which is due to a charge on the external surface of ZnS, the dependence of the magnitude of TAE on the illumination power is analogous to that characteristic of the barrier-trap mechanism for the photogeneration of non-equilibrium carriers in silicon substrate.

Thus, it has been shown that the measurement of TAE in the film structures is a very sensitive method to determine their charged state associated with the crystal structure, the conditions for its formation, and various external influences, for example, adsorption.

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