ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 6, № 2 (2005) С. 207-211

PHYSICS AND CHEMISTRY OF SOLID STATE
V. 6, № 2 (2005) P. 207-211

УДК 519.6:519.725

ISSN 1729-4428

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Charge Injection into Porous Silicon in the Temperature Range from 77 K to 400 K

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This article describes the charge injection into porous silicon structures fabricated by electrochemical treatment of 20 Ohm·cm p-type silicon. The I-V characteristics, photoluminescence spectra and lifetime kinetics have been studied at temperatures 77 K, 293 K and 373 K. Measurements show that the photoluminescence in porous silicon layers results from the recombination of electrons and holes captured in potential wells of various depth and shape; its intensity is controlled by nonradiative recombination on the wire boundaries. The charge flow in the Au(Al)-porSi-Si-Al structure results from the charge transfer in the metal – thin insulator – semiconductor configuration. The current is not restricted by the conductivity of insulating layers; it is restricted by the generation processes in the regions of space charge and semiconductor/ insulator interface due to large amount of defects with various ionization energies. Potential barriers at the surface of porous silicon are formed due to surface defects at the interface silicon wire/oxide; their generation tends to shift the surface potential to the intrinsic value.

Keywords: porous silicon, photoluminescence, surface defects.

Стаття поступила до редакції 09.03.2005; прийнята до друку 30.05.2005.

I. Introduction

Current carrier injection into porous silicon (PS) layers is one of the main processes that affect the efficiency of luminescence. To control the majority and minority carrier injection various methods can be used: choice of the contacting material with proper work function [1-3]; choice of the barrier structure type (Schottky diode [4], p-n junction [5,6], heterojunction [7,8]); technological variation of the physical parameters of interface (such as surface recombination rate [9], contact gap [10], bond type [11]). However these methods control the light emission efficiency indirectly, through the variation of carrier recombination rate. At present structures with stable photoluminescence are available. But the electroluminescence efficiency and, especially, stability are insufficient.

At present the processes of carrier injection and recombination in various PS structures are extensively investigated, and as a result adequate mechanisms are expected to be found and the efficiency of injection light emitters will be improved. The essence of the injection problem is the following. First of all the low resistivity contacts are of utmost importance to achieve a high level of minority carrier injection into the active region of the structure; suppression of the nonradiative recombination is also important due to the increase of the internal and external efficiency of the radiation sources.

The present paper deals with the analysis of charge flow processes, carrier injection and recombination processes in the barrier structure Au(Al)-PS-Si-Al.

II. Experimental

The Al(Au)-PS-Si-Al structures grown on p-Si by the standard electrochemical etching procedure [12] were investigated. After etching the surface was passivated. Due to the passivation the electrophysical and injection characteristics of the structure were stabilized. The PS layer width was about 1 μm. Frontal contacts were obtained by thermal evaporation of metal M (M-Al and Au) in vacuum and were deposited on the tilted PS sample through the mask of $0.04\ \mathrm{cm}^2$ surface area. Photoluminescence spectra and static I-V characterististics were measured by standard technique. To determine the effective lifetime of minority carriers τ the technique of the switch of the barrier structure from the forward to reverse bias [13] was used. All measurements were carried out in the temperature range from 77 to 400 K.

It is known that I-V characteristics of M-PS-Si-Al structure is essentially nonlinear (see, e.g.[1]). The present theories of I-V characteristics in barrier structures (including the ones with p-n- and heterojunctions) can not completely describe the experimental curves. For that type of barriers special theory of I-V characteristics should be developed, and to develop this theory deep comprehension of physical mechanisms of charge flow and injection in these systems is necessary. We hope that the joint analysis of integral and differential I-V characteristics will essentially improve the understanding of the abovementioned processes.

Application of differential approach to the I-V characteristics analysis [14] is aimed to reveal the fine structure of these curves. This approach is based on the determination of the dimensionless values $\alpha(V) = d\,\lg I/d\,\lg V = (dI/dV)/V/I)$ and $\gamma(V) = d\,\lg\alpha/d\,\lg V = (d\alpha/dV)/V/\alpha)$ The former value characterizes the power law dependence $I(V) = V^{\alpha}$, the latter one – the exponential law $I(V) = \exp(V^{\gamma})$. The treatment of the experimental I(V) dependences in the form of α(V) and γ(V) allows to describe this dependences adequately by a power law, when $\alpha = \text{const}$, and by an exponential low, when $\gamma = \text{const}$.

For the I-V characteristic of an ideal diode [15] $I = I_o\exp\{eV/\beta kT\text{-}1\}$ the obtained α and γ values are $\alpha = eV/\beta kT$; $\gamma = 1$, where I_o is the saturation current, k is the Boltzmann constant, T is the absolute temperature, β is the ideality factor. We can write for the ideality factor $\beta = eV/\alpha kT$. Note that for experimental I-V characteristics there is the necessity of fulfilment of the condition $\alpha = 0$ at $V = 0$.

III. Results and discussion

Fig. 1 shows stationary photoluminescence spectra of PS samples measured at 77 and 293 K. The fine structure of the bands (nonelementary bands) and large halfwidth (≈90 nm) are seen. The character, bands intensity and shape depend on temperature and excitation level. The above behaviour of the bands may be explained by the model of spatial quantization of charge carriers states. In this model the dispersion of quantum wires diameters that characterizes the deviation of this value from the statistical average wires size should be taken into account. The described behaviour of current and temperature dependences of the spectra can be also explained in the framework of the model accounting for the structural disorder and charged defects fluctuations that has been developed for heavily doped and compensated semiconductors [16]. Hereafter it will be shown that the second model is preferable in certain cases. In the latter model the charge carriers are captured and localized in the potential wells of various depths and shapes formed due to charge fluctuations, and thus, the charge carriers become spatially separated. More shallow wells contribute to the high frequency and more efficient recombination radiation while more deep wells cause the increase of low-frequency wing of the spectrum and the decrease of the recombination processes rate.

The lowering of the temperature down to 77 K caused the increase of the intensity (almost by a factor of 3) and halfwidth of the PS samples photoluminescence spectra as well as their spectral shift (by ~50 nm). The intensity of PS structure photoluminescence rised linear with the excitation intensity (in the limit of 1-1.5 orders of magnitude). All the above features are peculiar for the recombination processes involving at least one localized charge carrier.

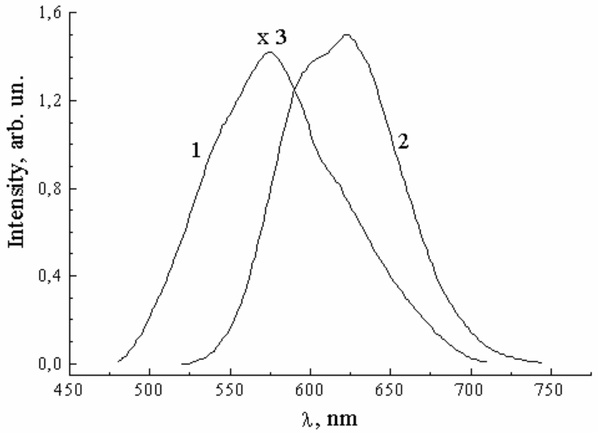


Fig. 1. Photoluminescence spectra of PS sample at 77 K (1) and 293 K (2).

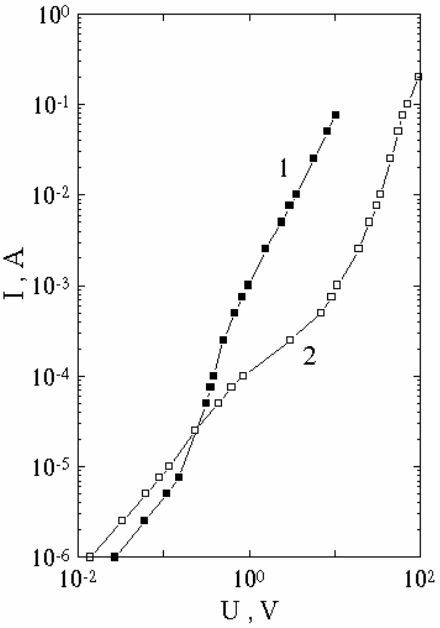
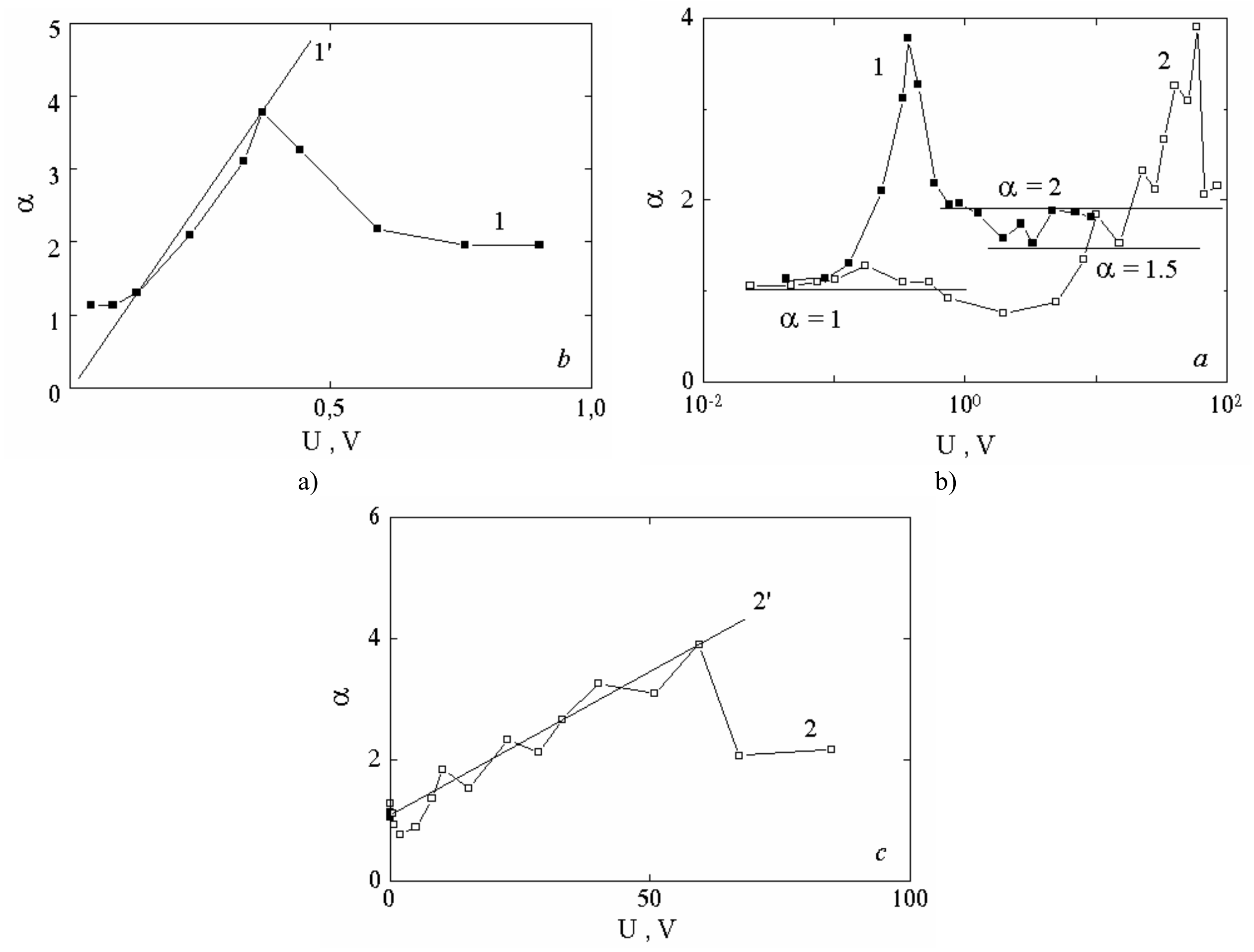


Fig. 2. Typical I-V characteristics of Au(Al)-PS-Si-Al structure: * – forward, o – reverse.

The above results correlate with the ones of photoluminescence kinetics measurements. Similarly to [16] the kinetics was nonexponential; this is peculiar for the recombination processes involving at least one localized carrier [16-18]. Naturally, we can discuss the lifetime of charge carriers under nonexponential relaxation only conventionally. There are special methods of relaxation curves treatment (e.g., the method of the expanded exponent [19], etc.). To determine τ we have used the direct measurements in accordance with the technique described in [13] (see below). Unfortunately the attempts to obtain the stable electroluminescence of PS in the barrier structures with contacts failed. To elucidate the reason of this phenomenon we have carried out the investigation of injection and recombination effects in the PS samples with contacts.



a) b)

c)

Fig. 3. Differential slope of I-V-characteristics: a) Al-PS-Si-Al structure :1 – forward bias, 2 – reverse bias; b) forward bias, stright line is approximation $\alpha(V) = 10 \cdot V$; c) reverse bias, stright line is approximation $\alpha = 0.05(V+20)$; d) Au-PS-Si-Al structure: 1 – 77 K, 2 – 293 K, 3 – 373 K.

Typical stationary I-V characteristics are shown in Fig. 2, and the dependences of their differential slope $\alpha(V)$ are presented in Fig. 3.

There are two quantitatively different sections on the direct branch of the I-V characteristic of Al-PS-Si-Al structure (the structure of the 1st-type). The initial exponential section with $\alpha(V) = 10$ V is shown in Fig. 3 b. The ideality factor is $\beta = 4.2$ in this case. The exponential section is followed by the one with $\alpha = 2$ that further transforms into $\alpha = 1.5$. The $\alpha = 2$ value corresponds to the regime of monomolecular recombination of charge carriers [20,21] when one type of carriers predominates. I-V curves measured at various temperatures are almost parallel in the second section range. The latter supports the field mechanism of charge flow in these structures. Probably it is the tunneling of charge carriers between silicon wires through SiO_x barriers. Similar mechanism is described in [22]. With the temperature increase I-V-curves shift to the high currents range: this behaviour also correlates with the results of independent measurements of minority carriers lifetime in the active region of PS-based structures (see below).

The described behaviour of the integral and differential I-V characteristics can be explained only in the framework of model of long n-p-p^+-junction (semiconductor with asymmetric contacts [23]). It is the case of double injection which is the intermediate one between the diffusion and drift currents. The diffusion and drift current components predominate at the opposite contact of the structure. This situation is observed when the carriers concentration in n- and p^+-regions drastically differ, the concentration of holes injected into the p-region being much higher than the equilibrium one. The latter correlates with the dependences of the carrier lifetimes (see below). In the case when $n \approx p$ the increase of the carriers injection level with the increase of the through current leads to the transition from the monomolecular recombination to the bimolecular one with $\alpha = 1.5$.

Determination of the voltage temperature coefficient showed that its value may be rather high (tens of mV/K) and increases with current causing the overheating of the structure. This effect should be accounted for at the investigation.

For the reverse branch of I-V characteristic (Fig. 2 and Fig.3 a, c) the $\alpha(V)$ curve exhibits the low voltage maximum with $\alpha_{max} = 1.3$ followed by the minimum with

$\alpha_{min} = 0.75$ and then by the exponential section $\alpha = 0.05(V+20)$ (Fig. 3 c). The lowering of the minority carriers injection level causes the transition from $\alpha > 1$ to $\alpha < 1$ at low bias values. With the increase of the injection level the dependence $I \sim \exp(V)^{0.5}$ is observed. This behaviour evidences that the Schottky emission with $\gamma = 0.5$ takes place. The comparison of forward and reverse I-V characteristics for the 1st-type structure is a one more corroboration of the model of asymmetric contacts with tunnelling charge flow mechanism at the forward bias and Schottky emission at the reverse bias.

Fig. 4 shows the dependences of τ on the injection level (the current in the PS-base barrier structure) measured at 293 and 363 K. It is seen that τ decreases with current. Such behaviour implies the nonlinear mechanism of charge carriers recombination and/or their recombination from the potential wells of various depth and shapes [18]. The latter mechanism is also supported by weak τ vs. current dependence. The decrease τ with T increase can be explained if one supposes the emergence (at certain current values) of nonlinear recombination mechanism (see above). Thus the existence of a series of relaxation times supports the idea of the recombination of localized, not free, charge carriers (at least one carrier, positive or negative, should be localized).

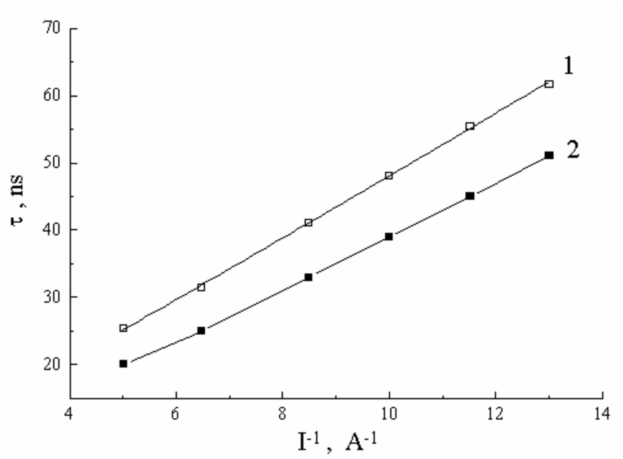


Fig. 4. The dependence of life time (τ) vesus injection level at 293 K (1) and 363 K (2).

The I-V- characteristic of Au-PS-Si-Al structure (the structure of the 2nd-type) at forward bias is similar to the one of the 1st-type structure only at low temperatures (77 K). In this case the initial exponential section with $\beta = 1$ is followed by the one with $\alpha = 1.5$ (bimolecular recombination) and then α increases again (Fig. 3 b). With the temperature increase the ideality factor value abruptly increases: $\beta = 11$ at $T = 293$ K and $\beta = 160$ at 373 K. While the bimolecular recombination ($\alpha = 1.5$, i.e. rather high injection of the carriers of both types) occurs at 77 K, the temperature increase causes the transition to monomolecular recombination ($\alpha = 2$, Fig. 3 d, domination of one type of carriers).

Finally we shall analyze the mechanism of band bending at the PS surface due to charging of this area. For this purpose the capacitor photo-induced voltage was investigated. Band bending in PS samples is rather small (≈20-30 mV), the depletion is sufficient to get the surface potential almost equal to the intrinsic one. Thus we achieved the self-compensation of charge at the PS surface due to the generation of a sufficient quantity of amphoteric defects necessary to move the Fermi level to the centre of the band gap [24]. Note that it is supposed that band bending remains unchanged both at the outer surface of PS and along the wire, i.e. inside the structure. At these conditions of charge flow the majority current carriers should tunnel through the additional (however small) potential barrier that originates from band bending in the space charge region (between the semiconductor and insulator). It is a one more corroboration of the field mechanism of charge flow in the structures under investigation.

IV. Conclusion

1. Photoluminescence in PS layers results from the recombination of electrons and holes captured in the potential wells of various depth and shape; its intensity is controlled by the nonradiative recombination at the wire boundaries. The arguments for this model are:

- the decrease of carrier lifetime with an increase of temperature and excitation level;
- the linear radiation intensity increases with temperature excitation intensity;
- the decrease of intensity with temperature caused by the temperature dependence of nonradiative recombination rate.

2. Charge flow in the system M-PS-Si-M results from the charge transfer in the system metal-thin insulator-semiconductor. The current is not restricted by the conductivity of insulating layers; it is restricted by the generation processes in the regions of space charge and semiconductor/insulator interface due to the large amount of defects with various ionizations energy.

3. Potential barriers at the surface of PS are formed due to surface defects at the interface silicon wire/oxide; their generation tends to shift the surface potential to the intrinsic value.

4. The Al(Au)-PS-Si-Al structure under investigation is described adequatly by the model of asymmetric contacts with a tunnelling charge flow mechanism at forward bias with monomolecular recombination and Schottky emission at reverse bias at room temperatures. Temperature decrease causes a transition to bimolecular recombination.

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Інжекція заряду в пористому кремнії в діапазоні температур від 77 K до 400 K

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