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A Scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences was held on 29 October 1997 at the P L Kapitza Institute for Physical Problems. Two papers were presented at this session:

(1) Kashkarov P K, Kamenev B V, Konstantinova E A, Efimova A I, Pavlikov L V, Timoshenko V Yu (Department of Physics, M V Lomonosov Moscow State University, Moscow) "Dynamics of nonequilibrium charge carriers in silicon quantum wires";

(2) Pulinets S A, Khegaĭ V V (Institute of Terrestrial Magnetism, Ionosphere and Radio Wave Propagation, Russian Academy of Sciences, Moscow), Boyarchuk K A, Lomonosov A M (Institute of General Physics, Russian Academy of Sciences, Moscow) "The atmospheric electric field as a source of variability in the ionosphere".

An abridged version of the papers is given below.

Dynamics of nonequilibrium charge carriers in silicon quantum wires

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1. Introduction

The technology of semiconductors perpetually tends to decrease the size of separate elements. At present, their sizes can be made as small as tenths of micrometer. As the nanometric range is approached, the physical principles of the functioning of semiconductor devices change significantly. The study of the fundamental properties of electron and hole behaviour in systems whose size in one, two or three directions is of the order of nanometers forms the basis of designing a new generation of devices.

The construction of solid-state nanostructures requires, as a rule, the use of high technologies. However, as early as in 1956 a sufficiently simple electrochemical method was suggested [1] to form porous silicon (PS), the nonetched sections of which represent the wires and clusters with a diameter d down to 1-4 nm [2]. Very intensive studies of the mechanical, structural, electrophysical, and optical properties of PS (see, for example, review [3]) began in 1990 after the efficient photoluminescence (PL) of PS at room temperature had been discovered in the visible region.

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The motive for these studies was the will to design an emitting device using one silicon integral scheme based on PS. However, the physical and chemical peculiarities of PS have not allowed this problem to be solved rapidly and the best laboratory samples have so far been characterized by a low efficiency of electroluminescence and a short service life. An appreciable degradation of the radiative properties of PS under optical, electron, and injection excitations is due to surface effects [3, 4]. Indeed, because of the extended surface (up to 800 m² g⁻¹ [2]), PS properties turn out to be very sensitive to ambient effects. However, this obvious shortcoming for applications turns into an advantage when studying fundamental processes in silicon nanostructures. The presence of pores accessible for surface molecules makes it possible to easily vary the composition of the outer layer of quantum wires and clusters thus cardinally changing the PS characteristics, including those of recombination. Such experiments allows one to formulate certain assumptions on the nature of luminescence in this material and in solid-state nanostructures as a whole [4].

Theoretical predictions slow that excitons with sufficiently large binding energies $E_{\rm exc} = 140-60$ meV can possibly exist in silicon quantum wires with a diameter of d = 1.5-3 nm [5, 6]. Based on this fact, many researchers relate the visible photoluminescence at room temperatures in PS with a radiative decay of excitons [3, 4]. However, direct optical observations of exciton states in PS are difficult due to a significant dispersion in the cross-sections of nanostructures, and, as a consequence, in variations of $E_{\rm exc}$. At the same time it is well known that the states considered are very sensitive to ambient dielectric properties around quantum wires. In particular, calculations show that when putting a quantum wire into a medium with a smaller permittivity, the exciton binding energy increases [7].

On general grounds, one should use the dielectric constant ε_d at a frequency of about E_{exc}/h when calculating E_{exc} . However, in an analysis of the medium polarization one should take into account that the effective mass of a hole in a quantum wire is much higher than that of an electron [5]. Thus, an electron moves in the field of an almost immobile hole, and in the expression for the interaction potential of charge carriers a value of ε_d close to the static one should be used. These qualitative considerations are confirmed by the results of our work [8], in which the degree of quenching of stationary PL on filling the pores of the PS sample by liquid dielectrics just correlated with the static value of ε_d .

In the present paper, which continues those studies, a quantitative description is given of the recombination processes in PS, with the PL measurements added with the monitoring of free-carrier IR absorption (FCA), both phenomena being observed with a time resolution. Utilizing two independent optical methods allowed us to watch

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simultaneously both radiative (PL) and nonradiative (FCA) recombination processes, which made it possible to draw a more definite conclusion about these processes. For a shorter presentation, the following structure for the paper was chosen: a model for the recombination processes in nanostructures, the experimental procedure, then the experimental results and a discussion.

2. A model for the recombination processes in PS nanostructures

We suppose that a PS nanostructure of high porosity can be represented in the form of a system of silicon wires with a sufficiently small diameter (1-5 nm) [2, 3]. Then it is assumed that in such wires, already at room temperature, photoexcited carriers form dynamically coupled subsystems of excitons and free electrons and holes. A radiative recombination results from exciton annihilation with a characteristic time τ_r , while a nonradiative recombination occurs only for free carriers on surface centres with a mean lifetime τ_{nr} . The kinetic equations for excitons (*N*) and free carrier pairs (*n*), with account of the experimental fact that the amplitudes of PL and FCA signals depend linearly on the excitation intensity, can be written as

$$\frac{\partial N}{\partial t} = Cn - AN - \frac{N}{\tau_r}, \qquad \frac{\partial n}{\partial t} = g - Cn + AN - \frac{n}{\tau_{nr}}, \quad (1)$$

where C is the probability of coupling free carriers in excitons, A is the probability of exciton thermal decay, and g is the electron-hole pair generation rate.

In the stationary case $\partial N/\partial t = 0$, $\partial n/\partial t = 0$ and from (1) follows that

$$N_{0} = \frac{gC}{\tau_{r}^{-1}\tau_{nr}^{-1} + A\tau_{r}^{-1} + C\tau_{nr}^{-1}},$$

$$n_{0} = g\tau_{nr} \left(1 - \frac{\tau_{r}^{-1}N_{0}}{g}\right).$$
(2)

Assuming that excitons with close binding energies E_{exc} contribute mainly to PL, we may relate the coefficients A and C:

$$\frac{A}{C} = \exp\left(-\frac{E_{\rm exc}}{kT}\right).$$
(3)

The value τ_r , according to calculations [5], weakly depends on the temperature over a broad range. The non-radiative recombination is an activation process [9] and its probability equals

$$\tau_{nr}^{-1} = \tau_0^{-1} \exp\left(-\frac{E_{\rm A}}{kT}\right),\tag{4}$$

where τ_0 is the minimum value of τ_{nr} . Substituting (3) and (4) into (2) yields

$$N_{0} = gC \left\{ \tau_{r}^{-1} \left[C^{-1} \tau_{0}^{-1} \exp\left(-\frac{R}{kT}\right) + 1 \right] + \tau_{0}^{-1} \exp\left(-\frac{E_{A} + E_{exc}}{kT}\right) \right\}^{-1},$$

$$n_{0} = g\tau_{0} \exp\left(\frac{E_{A}}{kT}\right) \left(1 - \frac{\tau_{r}^{-1} N_{0}}{g}\right).$$
(5)

These expressions permit us to analyze PL and FCA signal dependences on temperature and E_{exc} , which in turn

very sensitively depend on the ambient dielectric constant around the silicon wires. Indeed, a decrease in E_{exc} results in the stationary exciton concentration decreasing, and, as a consequence, in PL quenching, which we observed earlier in papers [4, 8].

The temperature dependences of N_0 and n_0 will obviously be different. Rising *T* always causes a decrease in the exciton concentration due to both increasing alternative recombination channel efficiency and thermal dissociation (we do not consider the case of helium temperatures when selection rules related with exciton state symmetries become essential [6]). In contrast, the $n_0(T)$ dependence under certain conditions can be nonmonotone: at sufficiently high E_{exc} the value of n_0 will grow with temperature due to thermal decay of excitons at high *T*, and fall due to activation of nonradiative recombination at low *T*. These qualitative considerations are fully consistent with the results of calculations using expressions (5) for fixed parameters τ_0 , τ_r , and E_A and three values of E_{exc} (Fig. 1).



Figure 1. Calculated concentrations of excitons N_0 (a) and free charge carriers n_0 (b) in PS are shown as a function of temperature for different values of $E_{\text{exc.}}$. Nonradiative recombination activation energy $E_{\text{A}} = 20 \text{ meV}$.

The kinetics of *N* and *n* decreasing after the excitation has stopped can be analyzed assuming a monoexponential time dependence:

$$N(t) = N_0 \exp\left(-\frac{t}{\tau}\right), \quad n(t) = n_0 \exp\left(-\frac{t}{\tau}\right).$$
 (6)

Substituting equations (6) into (1) at g = 0 yields for τ :

$$\tau = \frac{n_0 + N_0}{n_0 \tau_{nr}^{-1} + N_0 \tau_r^{-1}} \approx \begin{cases} \tau_{nr} \left(1 + \frac{N_0}{n_0} \right) & \text{at } \tau_{nr} \ll \tau_r ,\\ \tau_r \left(1 + \frac{n_0}{N_0} \right) & \text{at } \tau_{nr} \gg \tau_r . \end{cases}$$
(7)

It can be seen from equations (7) that, depending on the ratio τ_r/τ_{nr} , one can expect a directly opposite change for the relaxation time for PL and FCA signals by decreasing the fraction of excitons in the system of photoexcited charge carriers, i.e. when the ratio N_0/n_0 grows smaller.

3. Experimental procedure

PS samples were formed by electrochemical anodizing of monocrystal silicon plates of p-type with a resistivity of $\rho = 10$ Ohm cm in an HF-based solution [4]. To obtain nanostructures with a minimal cross-section, the samples were exposed to air for three months and were then etched in HF. According to Raman scattering and electron microscopy data, the value of *d* was about 2-5 nm. Measurements of IR absorption spectra show that the pore surface is mainly covered with hydrogen.

The PL and FCA kinetics were measured under pulse excitation of a nitrogen laser ($\lambda = 337$ nm, W = 0.1 mJ cm⁻², $\tau = 10$ ns). PL was registered in the range 350-850 nm by a photodetector with a response time of ~ 50 ns. FCA was observed with a time resolution of ~ 1 µs as a change in transmission by porous silicon of a He-Ne laser test beam ($\lambda = 3.39 \mu$ m). The nitrogen and helium-neon laser beams were focused at one point on the sample surface. The PL amplitude spectra reported in Section IV and PL and FCA amplitude dependences on temperature were measured with the same time resolution of ~ 1 µs.

PL and FCA signals were measured *in situ* for the samples in a vacuum (~ 10^{-4} Pa) or in a vapor-saturated atmosphere of organic materials. Benzene, acetone, ethanol, and methanol, whose static permittivities in the liquid state at 300 K are 2.5, 21, 24, and 33, respectively, were used. The moment of vapor condensation for these liquids was fixed by the sharp intensity increase of an Ar-laser test beam ($\lambda = 488$ nm) reflected from the sample surface [8].

4. Experimental results and discussion

The PS samples obtained were characterized by a rather weak PL (quantum efficiency less than 1%) in the range $\lambda = 500 - 800$ nm with a maximum near $\lambda_{max} = 650$ nm (Fig. 2). When making a comparison of the experimental data with the model predictions (Section 2), we shall assume the PL (I_{PL}) and FCA (I_{FC}) signals to be proportional to the exciton (N) and nonequilibrium free-charge-carrier pair (n) concentrations, respectively. We start with analyzing the experiments in a vacuum.

4.1 Temperature dependences of PL and FCA signal amplitudes

As was assumed in Section 2, at sufficiently low temperatures (80 K < T < 200 K) both the amplitudes $I_{PL}(0)$ and $I_{FC}(0)$ decrease with a rise in temperature (Fig. 3). The $I_{FC}(0)$ dependence on T in this range is well fitted by exponent (3) with $E_A = 20$ meV. It is this value that was used for calculations of nonequilibrium carrier concentrations in Section 2 (see Fig. 1).

In the framework of the model adopted (Section 2), the observed signal drop is due to a nonradiative recombination activation, and the parameter E_A determines the energy barrier to be overcome to capture the second charge carrier by the recombination centre [9]. The fact that the experimental dependence $I_{FC}(0)$ on T is described by a mono-



Figure 2. PL amplitude spectra of PS in a vacuum (1), vapors of benzene (2), ethanol (3), and methanol (4) at a temperature of T = 300 K.



Figure 3. Temperature dependences of PL (1) and FCA (2) signal amplitudes for PS in a vacuum. PL was observed at $\lambda = 650$ nm.

exponential function indicates the similarity of centres involved in the nonradiative recombination. The knowledge of the numerical value of E_A allows one to construct a detailed configuration diagram of the centre considered [9].

A comparison of the experimental values of $I_{\rm FC}(0)$ with the calculated free charge carrier concentrations n_0 for T > 200 K (Figs 1 and 3) yields the best match at $E_{\rm exc} = 150$ meV. In view of the weak dependence $n_0(T)$ in this temperature range, the quantity obtained can be considered only as an estimate, but nevertheless it is in reasonable agreement with the calculated $E_{\rm exc}$ for silicon wires (see Section 1 and Ref. [5]).

4.2 Temporal dependences of PL and FCA signals

The measurements carried out at 300 K suggest that, in accordance with data from Refs [3, 10], the kinetics of the PL decrease can be described by an expanded exponent

$$I_{\rm PL}(t) = I_{\rm PL}(0) \exp\left[-\left(\frac{t}{\tau_{\rm PL}}\right)^{\beta}\right],\tag{8}$$

with the parameters τ_{PL} and β being dependent on the recombination radiation wavelength λ . Figure 4 shows the curves $\tau_{PL}(\lambda)$ and $\beta(\lambda)$ for the samples studied. As is well known, the researchers connect relations like (8) with the cross-section distribution of nanostructures [3, 10]. From Fig. 4 it is seen that τ_{PL} falls within the microsecond range and that curves (8) approach the exponent for $\lambda \ge \lambda_{max} = 650$ nm (such an approximation was actually used in Section 2).



Figure 4. PL relaxation time τ_{PL} and the nonexponentiality parameter β as a function of recombination radiation wavelength for PS in a vacuum (×), benzene (\circ), and ethanol (\blacktriangle) at T = 300 K.

The FCA relaxation kinetics was also described by functions (8) with the parameters $\tau_{FC} \approx 9 \ \mu s$ and $\beta = 0.6$ (Fig. 5). These values correspond well to τ_{PL} and β for the PL signal in the maximum of the spectrum, which seems to be quite natural because according to our model [4], it is precisely excitons, producing radiation with $\lambda = \lambda_{max}$, that primarily contribute to the general recombination of nonequilibrium charge carriers.



Let us turn to analysis of data on the effect of dielectric ambiences on charge carrier dynamics in silicon nanostructures. In full agreement with the results of paper [8], changes in the PL and FCA characteristics were registered at the adsorbate vapor pressures $P_{\rm D}$ corresponding to a sharp increase of the coefficient of reflection from the PS surface under study. The latter suggests that the condensation of vapors of liquid dielectrics in pores and the formation of a liquid phase are the main effects of dielectric ambiences. The values of $P_{\rm D}$ were somewhat smaller than the corresponding saturated vapor pressures of the materials used, which is obviously due to capillary effects during molecular condensation. As for the case of a continuous excitation [8], the dielectric ambient effect on PL and FCA was practically fully reversible in the bleeding-in pumping-out cycles. So with account of data from Ref. [4] we believe that the above effect to the first approximation is solely due to the change of the dielectric constant ε_d in the ambience around the silicon nanostructures.

4.3 Influence of dielectric ambiences on the PL and FCA amplitudes

As follows from Fig. 2, the PL amplitude spectra remain practically unchanged during the filling of pores by benzene. The bleeding-in of vapors of materials with a high ε_d in the liquid state resulted in PL quenching by a slight deformation of the spectrum (Fig. 2). In the latter case a notable increase of the FCA amplitude was observed. This is clearly seen from the diagram in Fig. 6. For comparison, in the same diagram we plot the data for single-crystal silicon having the same parameters as used as a substrate in PS formation. The crystal was processed in HF without current passage. As can be seen from Fig. 6, any change in the FCA signal parameters during the ethanol saturated vapor bleeding-in was absent in this case. This serves as an additional confirmation of the fact that the adsorption of the organic substances considered does not alter the parameters of the surface recombination centres, and that in the case of PS the effect is totally due to the dielectric properties of these substances. The observed phenomenon is fully explained in the framework of the model proposed. Indeed, the filling of pores by a medium with a high permittivity decreases E_{exc} , which in turn causes the exciton concentration N to decrease at a fixed temperature. Although the total number of photoexcited carriers apparently changes insignificantly, since most of them recombine nonradiatively, a redistribution between subsystems of coupled and free charge carriers nevertheless occurs in favour of the latter. This gives rise to an increase of the FCA signal.



Figure 6. Diagrams for $I_{FC}(0)$ amplitudes and FCA signal relaxation times τ_{FC} for PS (at the bottom) and c-Si (at the top) in a vacuum and in vapors of benzene or ethanol.

The absence of a change of the PL amplitude spectral maximum position during variations of dielectric ambience around silicon wires (see Fig. 2) seems somewhat unexpected here. It should be expected that by decreasing E_{exc} the PL spectrum shifts towards larger hv. Apparently, the effect observed can be explained by the fact that the polarization of the medium by the electric field of coupled carriers changes not only E_{exc} but also the forbidden band width E_g of the silicon wire near the exciton [11]. In addition, the changes of E_{exc} and E_g are comparable and have a negative sign for $\varepsilon_d > \varepsilon_{\text{Si}}$. Consequently, the exciton PL band position $hv_{\text{exc}} = E_g - E_{\text{exc}}$ will be almost unchanged. We recall that

during measurements of stationary PL spectra [4] the position of the maximum of a nonuniformly broadened line under the filling of pores by dielectric liquids shifts to the 'blue' side. This is apparently not due to a decrease in E_{exc} , but because of a decrease in the relaxation time of nonequilibrium charge carriers mainly in nanostructures that contribute to the lowenergy part of the PL spectrum (see Section 4.4).

4.4 PL and FCA signal kinetics for PS in a dielectric ambience

Experiments have shown that the bleeding-in of a saturated vapor of benzene does not significantly affect the PL signal relaxation in PS (see Figs 4 and 6). This accords with the concepts considered in Section 2. Indeed, the dielectric constant of benzene is small and apparently the ratio of free charge carriers to those coupled in excitons does not vary significantly [see equation (7)]. Rather unexpectedly, at first glance, was the effect of the change of kinetic characteristics of PL and FCA after the filling of pores with mediums possessing high values of ε_d . The decrease of the radiative recombination efficiency was accompanied not by a growth, but by a decrease in the PL and FCA signal relaxation times (see Figs 4 and 6). In the case of PL the effect was more pronounced for the long-wave parts of the spectrum corresponding to the contribution of nanostructures with larger cross-sections (see Fig. 4). For all parts of the PL spectrum a decrease in the parameter β was observed, which indicates an increase in the degree of inhomogeneity of the PS nanostructure system.

The changes in the kinetic parameters of PL and FCA observed after the filling of pores with mediums featuring a high value of ε_d can be explained in the framework of the model considered as follows. The small efficiency of PL in the PS samples studied obviously implies the following relation between the radiative and nonradiative recombination times: $\tau_r > \tau_{nr}$. This relation is enhanced for nanostructures with larger diameters due to an increase of τ_r [5, 6]. Therefore, for just such structures, in accordance with equations (7), the relative decrease in exciton concentration must cause a decrease of the PL and FCA signal relaxation times. In the measurements of FCA, it is impossible to separate the contributions from nanostructures with different sizes, so we fix some average time τ_{FC} , but for PL the effect of the dependence of the τ_{PL} relative change on wavelength, predicted by the model, is registered quite well (see Fig. 4).

5. Conclusions

In the present paper a model for recombination processes in silicon nanostructures is developed, which assumes the presence of dynamically coupled subsystems at room temperature: free charge carriers and excitons. The data obtained for PS by time-resolved measurements of photoluminescence and free carrier absorption can be explained by the model proposed. In particular, the temperature behaviour of the PL and FCA signals, as well as the dependences of the amplitude and temporal characteristics of these signals on the dielectric properties of the ambience around the quantum wires of the PS, are in full agreement with the model's predictions.

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The atmospheric electric field as a source of variability in the ionosphere

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1. Introduction

The terrestrial ionosphere is very sensitive to exposure to external factors, so its characteristics are subjected to regular and irregular variations. Ordinarily, the regime of the ionosphere is considered solely in connection with solar and cosmic effects [1]. However, some studies indicate that short-term anomalous variations appear in the ionosphere even under the constancy of external factors [2]. It is natural to suppose that the reason for these variations is internal, i.e. the ionosphere also reacts to the processes occurring in the troposphere and on the surface of the Earth. Volcanic activity, earthquakes, cyclones, thunder storms, explosions, various contaminations in the troposphere — all of them have an effect on the ionosphere. At present, this problem is being actively studied since there is experimental evidence for this relation [3, 4]. The results of these studies open up the prospect of constructing a self-consistent model for the electrodynamic interaction between the troposphere and ionosphere.

The purpose of the present paper is to study one possible mechanism for the influence of geological and anthropogenic factors on tropospheric and ionospheric processes resulting from electrostatic fields.

2. Tropospheric processes

Consider some processes changing the gradient of the electrostatic potential of the Earth in the troposphere.

2.1 Dust and sand storms

Dust has an effect on the atmospheric electric field, since the attachment of small ions and friction result in the dust particles acquiring an electric charge. It is established that most of large ions is negatively charged and that bigger aerosol particles seem to absorb negative ions more easily [5]. As noted in paper [6], during dust storms the maximal deviation of the atmospheric electric-field-potential gradient from the unperturbed value ranged from +15 to