Investigation of pulsed photoluminescence of *a*-Si:H subjected to intense picosecond excitation

A. M. Danishevskii, V. Latinis, M. M. Mezdrogina, V. Kh. Kudoyarova, and E. I. Terukov

Ioffe Physicotechnical Institute of the Russian Academy of Sciences, Politekhnicheskaya 26, 194021 St. Petersburg, Russia

(Submitted 9 March 1993; revised 11 August 1993)
Zh. Eksp. Teor. Fiz. **104**, 4031–4041 (December 1993)

We measure photoluminescence spectra on *a*-Si:H samples under intense picosecond excitation and observe narrow intense spectral bands at times immediately following the excitation. These bands are due to lasing. Their energies are determined by the film surfaces, which act as a selective cavity. At later times, the inversed population dissipates, the amplification in the system decreases, and the nature of the spectra changes. In particular, the narrow bands are no longer observed.

INTRODUCTION

Photoluminescence of amorphous hydrogenated silicon has been investigated in detail under both continuous and pulsed excitation.[1,2] The ordinary spectrum of characteristic luminescence is a structureless spectral band 0.22–0.25 eV wide with a maximum near 1.33–1.35 eV (80 K). For short-pulse excitation, the maximum of the characteristic photoluminescence band appears near 1.4 eV, and its short-wave tail reaches 1.6 eV for substantial levels of excitation.[2] Studies of photoluminescence, in combination with ESR and photoconductivity, allow a generally accepted recombination model to be constructed for *a*-Si:H. At low temperatures ($T < 60$ K), an electron and a hole arising from absorption of an optical quantum are believed to be captured instantaneously ($t \leqslant 10^{-12}$ s) to localized states of the band tails. As this is taking place, the steady-state filling of states in the tails, hence the photoluminescence spectrum, are determined by the competition between charge carrier hops to lower energy states and radiative tunnel recombination processes. It is commonly supposed that twin radiative recombination is preferentially realized when the excitation level is relatively low so that the mean distance between the twinned electron and hole is considerably smaller than the mean distance between nearest localized photocarriers. In the opposite case, which correspond to a very high excitation level, interpair recombination may dominate. In the region of moderate concentrations, photostimulated diffusion may be of considerable importance.[3] In essence, the recombination proves to be twin, but the excess carrier concentration is determined by interpair processes.

In Ref. 4, the steady-state low-temperature photoluminescence spectrum was calculated for the case of interpair recombination assuming that the luminescence quantum yield is 100%. The photoluminescence spectrum was shown to shift to the higher energies as the deeper localized states in the band tails are filled and the generation rate increases. The shape of the spectrum remains practically unchanged. The short-wave spectrum shift was observed earlier[2,5] for short-pulse excitation of photoluminescence. In the latter case, however, the spectra were somewhat broadened in addition.

As for the kinetic characteristics of the photoluminescence of amorphous silicon, they are complicated and depend largely on the photoexcitation properties. The distribution of the typical radiative recombination times has been calculated in a number of papers, and was found to be very broad (10^{-8}–10^{-2} s) with a maximum near 10^{-5}–10^{-4} s (Ref. 2). However, still faster photoluminescence decays were observed.

Orlowski and Sher[6] studied the decay of integral photoluminescence excited by picosecond pulses, using a streak camera with an optical multichannel analyzer sensitive in the 1.5–2.1 eV interval. Rapid photoluminescence decay in the 0–70 ps range was observed. The decay rate was substantially lower at longer times. The authors reasoned that the radiative recombination of localized and delocalized pairs with the shortest separation should be responsible for such short signals. The major contribution to the signal at the early photoluminescence stage is related to the 1.8–2.1 eV spectrum range, since the photoluminescence pulse was shortened by a factor of three, when the spectrum was bounded above by a 1.8-eV filter.[1)]

EXPERIMENTAL DATA

As in Ref. 6, *a*-Si:H photoluminescence was excited by single high-power picosecond (35 ps) 2.33-eV pulses from a frequency-doubled YAG:Nd laser with 2 Hz repetition frequency.

The *a*-Si:H samples were obtained in a tetrode system in a chamber with a high-frequency glow discharge by decomposition of pure silane. The substrate temperature was 280 °C. In the experimental work cited, *a*-Si:H films deposited on tarnished substrates were used for photoluminescence studies to eliminate interference. However, in the present work, the films were deposited on polished plates of fused silica.

The optical widths of the band gap were 1.85–1.9 eV in the samples used for the experiment. The Fermi energies, defined as the activation energies in the temperature de-

 1063-7761/93/120944-06$10.00

pendence of the conductivity, were $E_F=0.8$–0.95 eV. The densities of the intrinsic defects were less than $8\cdot 10^{15}$ cm^{-3}.

These photoluminescence results were obtained in the M912 sample with the lowest defect concentration ($N_d=3\cdot 10^{15}$ cm^{-3}), the smallest the Urbach tail energy parameter ($E_u=50$ meV) in the absorption spectrum, and an activation energy of 0.92 eV. The photoconductivity spectra were measured for all the samples in slab geometry (the film thickness was $d=0.8$–1.0 μm and the contact separation was 4 mm), and only those were selected for the photoluminescence measurements, which did not exhibit a significant drop in photoconductivity below 5 eV, i.e. with small surface recombination rate. This suggests that the samples lacked columnar structure[2)]. When measuring photoluminescence, we mounted the samples on a nitrogen vacuum cryostat cooling finger. The sample temperature in the experiments was about 80 K. The measurements were performed in the reflecting geometry. The photoluminescence spectra were recorded using an MDR-2 monochromator with an FEU-83 photomultiplier. To avoid detecting scattered light, we used colored glass filters to cut off the spectrum range $\hbar\omega > 2.1$ eV. The signal pulses from the photomultiplier were fed to a broad-band amplifier with a transmission band of $(0.7$–$10)\cdot 10^6$ Hz and then to a V5-9 sampling converter. The digitized signals from the latter passed through CAMAC blocks and entered a DVK-2 microcomputer. When recording the spectrum, each point was obtained by averaging over 30–40 pulses on a specified interval of the amplitudes of the exciting pulses.

Note that the photoluminescence spectra depended sensitively on the light intensity at the sample because of the very high photoexcitation level (up to $\sim 10^{21}$ cm^{-3}) used in the experiments. Since the intensity was distributed nonuniformly over the light spot, the spectrum shape could vary with the width of the monochromator input slit. In addition, the spectra obtained with narrow slits were recorded with large fluctuations and poor reproducibility due to variations in the light spot shape from pulse to pulse. All the experiments were thus performed with 1.2 μm slit width corresponding to ~ 5 nm resolution of the monochromator. The light spot size at a sample was less than 0.7–0.8 mm. In this case, the contribution to the spectrum results from integration over the area of the illuminated spot.

During the experiments we attempted to measure the photoluminescence signals with optical gating by the first harmonic radiation of the picosecond laser used (35 ps). As in Ref. 6, this experiment was conducted in the range of quantum energies 1.8–2.1 eV. However, the fraction of radiation emitted by the sample in the time interval under consideration appeared to be too insignificant, and the sensitivity of the signal detection system proved to be insufficient for reliable measurement.[3)] The gating of the electric signal from the photomultiplier was therefore performed after amplification. The amplifier transmission band had to be bounded from above by a frequency of 10^7 Hz in order to avoid recording short-pulse noise from the electro-optical shutter selecting a single picosecond laser pulse.

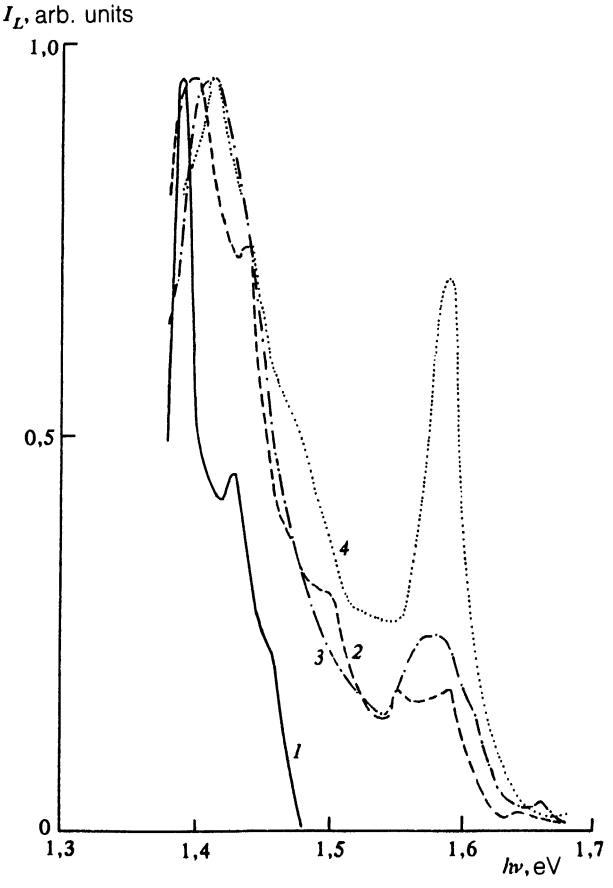

FIG. 1. Pulsed photoluminescence spectra of the M912 sample recorded with a gate time delay of 80 ns. The mean energies of the excitation pulses are: *1*—1.1 μJ; *2*—2.2 μJ; *3*—6.45 μJ; *4*—17 μJ; $T=80$ K.

Therefore, the transient characteristic of the amplifier of the photomultiplier did not allow us to specify the true gating time of a photoluminescence optical pulse. Nevertheless, the spectra recorded with different sample delays in the V5-9 converter were essentially different. The zero-time point was determined from the time at which detection of scattered pump light ($\hbar\omega=2.33$ eV) began.

The photoluminescence spectra of the M912 sample for four values of the exciting pulse energy are presented in Fig. 1. The spectra were recorded under the previously described conditions. All four spectra were measured with a delay of 80 ns relative to the beginning of the pulse. As seen in Fig. 1, spectrum 1 obtained at the minimum intensity of the exciting pulses was substantially narrower than the data presented elsewhere (see, for instance, Refs. 2 and 5). The width of the band with a maximum at 1.39 eV was found to be less than 20 meV. Spectrum 2, recorded at a higher intensity of excitation, is significantly broader. Its maximum and the short-wave part of the spectrum are shifted towards higher energies ($\hbar\omega_m=1.405$ eV). The main band is inhomogeneously broadened. We may suppose that this is a result of a superposition of two narrower bands with energies of 1.395 and 1.41 eV. As in spectrum 1, there are other small maxima in spectrum 2. Spectrum 3,

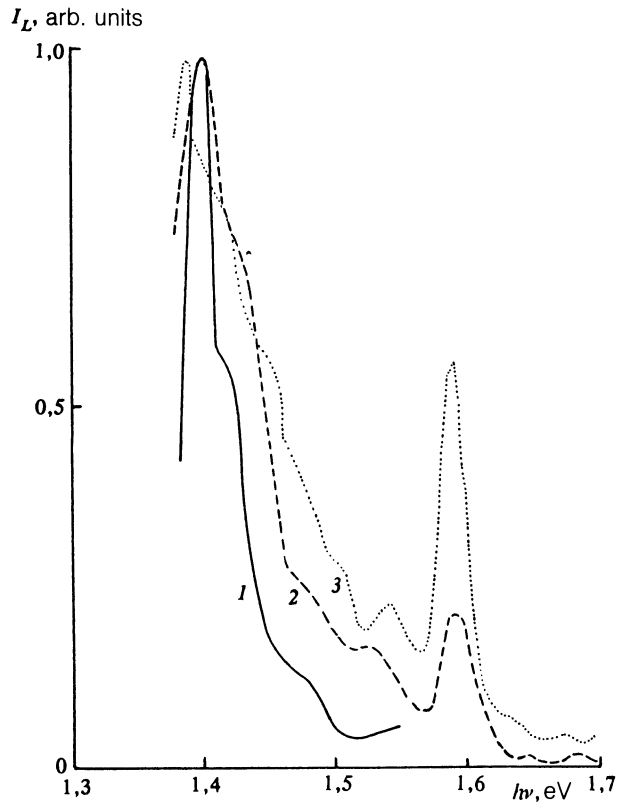

FIG. 2. Pulsed photoluminescence spectra of the M912 sample recorded with a gate time delay of 180 ns. The mean energies of the excitation pulses are *1*—1.5 μJ; *2* 3.8 μJ; *3*—34 μJ; $T=80$ K.

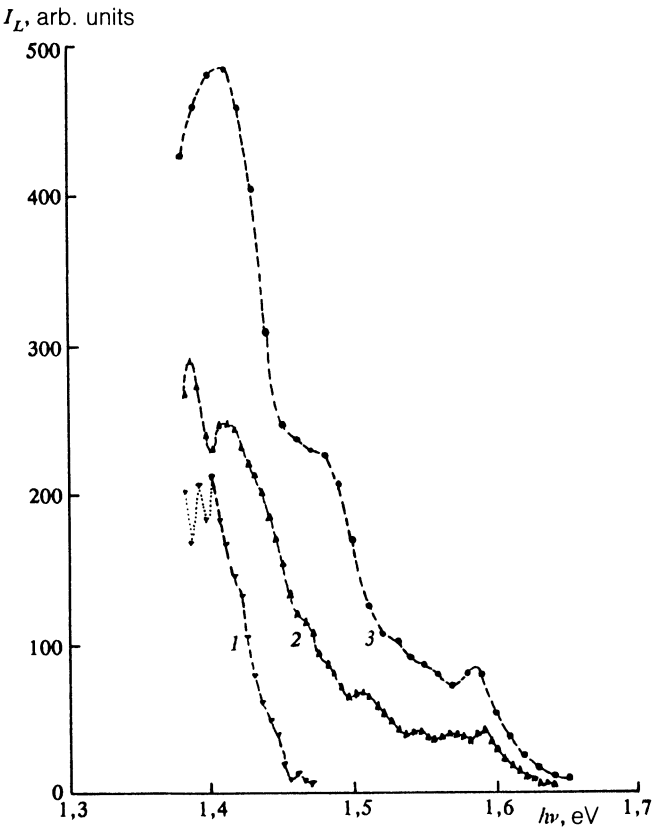

FIG. 3. Pulsed photoluminescence spectra of the M912 sample recorded with a gate time delay of 580 ns. The mean energies of the excitation pulses are *1*—1.5 μJ; *2*—4.1 μJ; *3*—9.9 μJ; $T=80$ K.

obtained at still higher excitation intensity, is broadened still further. Its main maximum is located at an energy of 1.415 eV, and a fairly broad emission band arises near 1.59 eV. The first maximum of spectrum 4 on the long-wave side also has an energy of 1.415 eV. Furthermore, this band has a shoulder at $\hbar\omega > 1.46$ eV, and a narrow intense peak appears now at an energy of 1.59 eV. Apart from unusually narrow spectral bands, our attention was engaged by superlinear growth in the amplitude of the spectrum line near 1.4 eV at low intensities and flattening of this dependence when the excitation level was increased.

A set of spectra obtained on the same sample but with longer gate time delays t_z are presented in Figs. 2 and 3. At $t_d=180$ ns (Fig. 2), the spectrum features are differ little from those presented previously. The minimum excitation intensities are somewhat greater in this case than in Fig. 1, and the main narrow band of spectrum 1 (Fig. 2) is broader here. Its maximum is at 1.4 eV and it does not shift when the pump intensity is increased slightly (by a factor of 2.5 spectrum 2). True, the 1.4-eV band is broadened still further in spectrum 2. There are similar features in the form of shoulders in both spectra, and a rather intense narrow band appears in spectrum 2 even at $\hbar\omega=1.59$ eV. In spectrum 3, recorded at a much higher intensity, this band grows in amplitude still further and becomes narrower. The first maximum of spectrum 3 was shifted towards 1.39 eV, its width being less than those of spectra 1 and 2.

The character of the spectra obtained with 580 ns gate delay turned out to be quite different. No clearly defined narrow peak near 1.4 eV is present even at low excitation intensities. At higher intensities, a poorly defined small peak in the vicinity of 1.58–1.59 eV appears. However, the general trend of shifting the short-wave part of the spectrum towards the higher energies with excitation level increasing remains.

DISCUSSION OF THE RESULTS

The features of the spectra obtained and their comparison with analogous spectra of Ref. 5, where intense picosecond excitation was also used but *a*-Si:H films were deposited on tarnished substrates, imply that the presence of reflecting film surfaces forming a cavity could essentially affect the spectra. Another reason for the complicated structure of the spectra could be associated with the presence of singularities in the density of states in the band tails for certain *a*-Si:H samples.

To clarify the influence of the factors outlined, we measured transmission spectra for all the samples. A nearly parallel light beam from a DMR-4 monochromator was produced for this purpose, and the slits were adjusted so that the spectrum line widths were less than 1 meV. Pho-

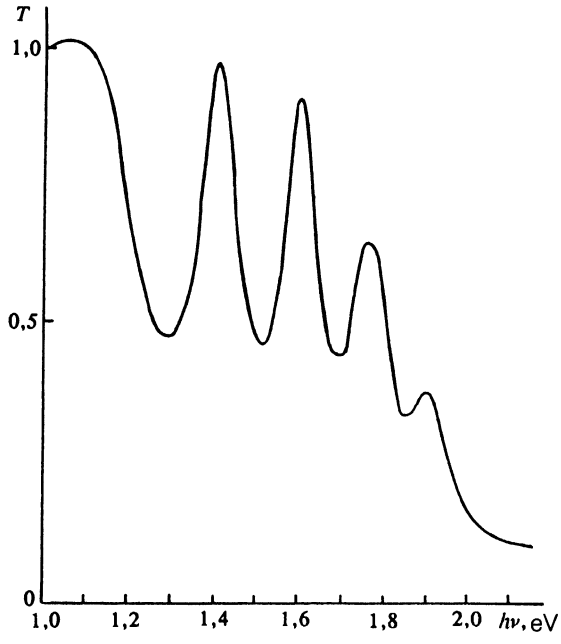

FIG. 4. Transmission spectrum of the M912 sample, $T=300$ K.

toconductivity spectra were also measured in accordance with the constant photocurrent method (CPM spectra) for all the samples in order to study special features of the density of states.

The transmission spectrum and the CPM spectrum of the M912 sample are presented in Figs. 4. and 5, respectively. It can be seen that in the vicinity of 1.4 and 1.59 eV interference maxima are present in the transmission spectrum. It is these energies that correspond to the narrow bands appearing in the photoluminescence spectrum.

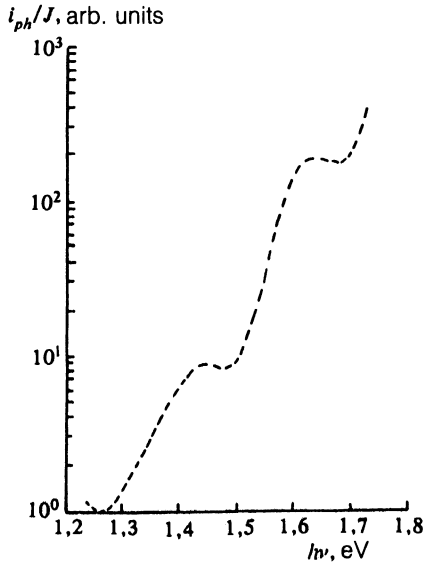

FIG. 5. CPM spectrum of the M912 sample, $T=300$ K.

Other samples exhibited similar behavior. Since the films were of different thicknesses, one or two interference maxima in the transmission spectrum could fall within the region of photoluminescence spectrum being recorded. In each case, the photoluminescence spectrum represented these features adequately. But should we just consider this behavior of the photoluminescence spectra to be associated with the occurrence of interference? In our opinion, this is not the case. First, the luminescence bands in a number of the cases mentioned are substantially narrower than the maxima in the transmission spectra, which indicates that amplification is present in the system of recombining localized photocarriers. It should be also stressed that the photoluminescence spectra were recorded with rather wide slits (~ 5 meV) of the spectral instrument, and this should weaken interference effects in the absence of amplification resulting in spectrum narrowing. The behavior of the 1.59-eV band for the M912 sample as a function of increasing excitation intensity is especially typical. A significant narrowing of this band is clearly seen as the carrier generation rate increases. And finally, the fact that the narrow bands no longer appear either at 1.4 or at 1.59 eV for large time delays (580 ns) indicates the inverted population in these states dissipates and the amplification in the system decreases with time. In view of all these facts, we are forced to the conclusion that we are dealing with the laser effect. This is all the more so because, as the estimates show, the excess concentration of charge carriers generated in a single pulse significantly exceeds 10^{19} cm^{-3} in the present experimental results even at minimum pump intensity. Maximum excitation levels reach 10^{21} cm^{-3}. In the vicinity of the energy values listed above, the film is a single-mode (as far as longitudinal modes are concerned) cavity with rather small losses. This assists the release of these energies in the superluminescent spectrum.

The significant shift of the spectra to higher energies as the pump level increases and the very high excessive concentration of carriers excited in a single pulse suggest that interpair recombination dominates in this case. Such recombination occurs, when the mean distance between the nearest localized photocarriers is smaller than the distance between twin electron and hole. Such recombination assists excitation exchange between the states nearest in energy and involving a large number of pairs in the process of stimulated recombination in the vicinity of the specified radiation band.

Two processes take place as the pump intensity increases. On the one hand, higher and higher energy states are filled, primarily in the tail of the conduction band, and the spectrum accordingly broadens towards the higher energies. On the other hand, the amplification as the lasing transitions begins to saturate (in particular, in spectrum 1 of Fig. 1 on the 1.39-eV transition). Inversion occurs at the low-lying transitions with slightly higher energies falling within the band of the selective cavity. Therefore, the spectral band near 1.4 eV (Fig. 1) broadens and shifts to the short-wave side. At high excitation intensities, when still higher states become filled, the narrow emission band near 1.59 eV starts to radiate. This band falls within the next

transmission interference maximum of the cavity formed by the film surfaces.

Summing up, we emphasize once more that the dynamics of the photoluminescence spectral variation as the excitation intensity and the instant of their detection vary in these experimental results allows us to conclude that the principal signs of the laser effect are present. It should be noted that similar results were obtained on several samples.

At the same time, it should be said that because of the small film thickness (~ 1 μm), the active medium must have a rather high gain coefficient to meet the ordinary conditions of lasing. The power gain coefficient in the active medium with a cavity with 100-% inversion and zero losses can be written as

$$G=\frac{(1-R)^2K}{1-2RK\cos(4\pi l/\lambda)+R^2K^2}, \qquad (1)$$

where $K=\exp(\alpha l)$, R is the reflection coefficient of the film (both surfaces are supposed to reflect radiation perfectly). The condition $RK<1$ was used in the derivation of (1). At resonance, i.e., for $\cos(4\pi l/\lambda)=1$, we have

$$\cos(4\pi l/\lambda)=1; \quad G=\frac{(1-R)^2K}{(1-RK)^2}. \qquad (2)$$

From (2), the gain coefficient α_0 necessary for the onset of lasing can be estimated. For $R=0.285$ and $l=10^{-4}$ cm we have $\alpha_0 \geqslant 1.9\cdot 10^4$ cm^{-1}. The gain coefficient of the lasing transition cannot exceed the absorption coefficient for the same optical photon energy. As for the absorption coefficients in a:SiH for energies $h\nu=1.4$ and 1.59 eV, they are rather small and, in particular, much less than the α_0 value estimated previously. So the gain coefficients obtainable on these transitions seem to be insufficient to produce lasing. It is thus necessary to assume that the spectrum of the electron state density changes under the action of intense short-pulse pumping to explain the results observed in the experiment.

Since the appearance of the photoluminescence spectra presented is closely related to the optical pathlength in the cavity, the variation in the refractive index (nonuniform over the area of the illuminated spot on the sample) under the action of intense pulsed photoexcitation may also have some effect on the spectrum structure, even resulting in shifts of certain emission band energies, variations in their shapes, and so on. However, it is not possible, in our opinion, to use this mechanism to explain the whole combination of the phenomena observed.

We have mentioned the possibility that certain features of the density of deep tail states can be revealed in the stimulated emission spectra. These features were observed in a-Si:H samples in some cases from CPM spectra. A CPM spectrum of the M912 sample is shown in Fig. 5. The maxima observed in this spectrum are somewhat shifted in energy with respect to the maxima in the transmission spectrum and are related, in our view, to interference effects in the photocurrent spectrum. In a number of other samples, features in the CPM spectra were observed bearing no relation to interference. In these cases additional

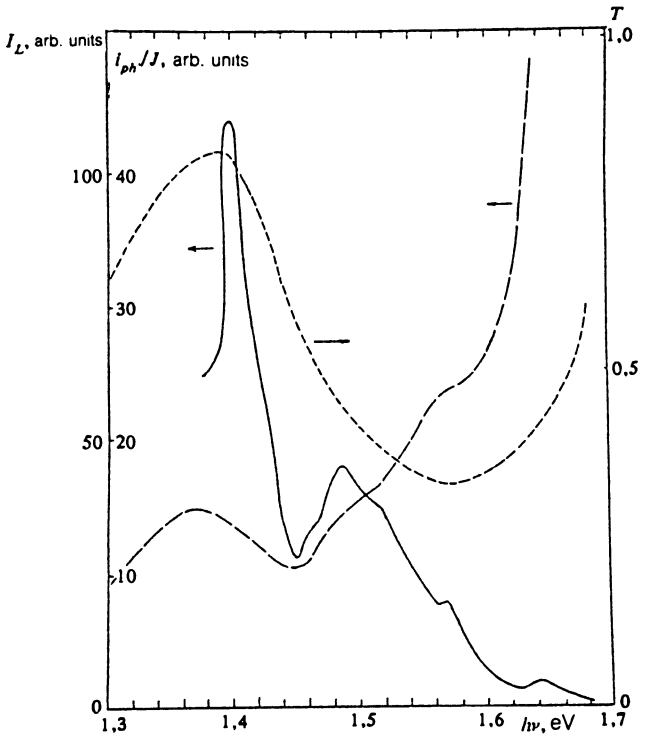

FIG. 6. Pulsed photoluminescence spectrum of the M930 sample recorded with a gate time delay of 180 ns. The mean energy of the excitation pulses is 1.5 μJ. $T=80$ K. Transmission spectrum of this sample and its photosensitivity spectrum in the "constant photocurrent mode" are shown by the dashed lines.

structure was present in the photoluminescence spectra under intense picosecond excitation. In Fig. 6, a photoluminescence spectrum of the M980 sample recorded at relatively low excitation levels is given. This film is thinner than the M912 sample, and only one maximum of its transmission spectrum with an energy of 1.4 eV falls within the recorded interval of the photoluminescence spectrum. A narrow maximum with an energy of 1.4 eV is seen in the photoluminescence spectrum as well. It is much narrower than in transmission. But there is also a wide band in the photoluminescence spectrum with a maximum at 1.49 eV unrelated to the selective cavity. In energy, it corresponds to several overlapping bands in the CPM spectrum of this sample.

In addition to the most prominent spectral bands of photoluminescence, there are small peaks, shoulders and other features in virtually all the photoluminescence spectra obtained, including the best sample M912. It is possible that they are also related to the characteristics of the density of states function in the tails of a-Si:H bands. In some of CPM spectra presented in Ref. 8, the parts of the spectra corresponding to deep states in the tails possess a quasi-discrete structure. The authors of Ref. 8 practically do not comment on this problem. As for our CPM spectra, they were recorded point by point, and such structure was not

observed. This question needs a more extensive study.

The authors are grateful to V. I. Perel' and E. L. Ivchenko for discussion and valuable advice.

[1)]The authors of Ref. 6 claim that they eliminated short-wave fluorescence associated with surface contamination. From the data of Ref. 7, it is believed that they worked with columnar samples, and the nature of this "above-band" radiation may be related to quantum-size effects.

[2)]Short-wave surface fluorescence was not observed from these samples even at very high excitation levels.[7]

[3)]This result is in contradiction with the data of Ref. 6. However, it is difficult to comment because *a*-Si:H samples of different quality were used in the present work and in Ref. 6.

[1]R. A. Street, Adv. Phys. **30**, 593 (1981).

[2]C. Tsang and R. A. Street, Phys Rev. B **19**, 3027 (1979); T. M. Searle, T. S. Nashashibi, I. G. Austin, R. Devonshire, and G. Lockwood, Phil. Mag. B **39**, 389 (1979).

[3]E. D. Baranovskii, E. L. Ivchenko, and B. I. Shklovskii, Zh. Eksp. Teor. Fiz. **92**, 2234 (1987) [Sov. Phys. JETP **65**, 1260 (1987)].

[4]A. G. Abdukadyrov, S. D. Baranovskii, and E. L. Ivchenko, Fiz. Tverd. Tela **24**, 136 (1990).

[5]W. A. Wilson, P. Hu, J. P. Harbison, and T. M. Jedju, J. Non-Cryst. Sol. **59/60**, 341 (1983).

[6]T. E. Orlowski and H. Sher, Phys. Rev. Lett. **54**, 220 (1985).

[7]A. M. Danishevskii, V. Latinis, M. M. Mezdrogina, *et al.*, Fiz. Tekhn. Poluprovodn. **27**, 913 (1993) [Semiconductors **27**, 495 (1993)].

[8]J. Kočka, M. Vaneček, and A. Tříska, in *Amorphous Silicon and Related Materials*, Ed. H. Fritzsche, World Scientific, Singapore, pp. 189–222 (1991).

Translated by A. M. Mozharovskii

This article was translated in Russia and is reproduced here the way it was submitted by the translator, except for stylistic changes by the Translation Editor.