COLLECTIVE PROPERTIES OF EXCITONS IN SILICON

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Recombination radiation of silicon has been investigated at high injection levels. It is shown that at high densities of excitons, their collective interactions become important, leading at low temperatures (less than 20°K) to the formation of exciton "drops." At higher temperatures the formation of associations of excitons, drop embryos, becomes possible.

CONSIDERABLE interest has developed recently in the properties of a system of excitons of high density. At exciton concentrations such that the distance between them becomes of the order of their radius, there must arise, in the opinion of Keldysh[1], a collective exciton state of the liquid type.

In the study of the collective properties of excitons, one of the fundamental problems is the question of the dominant character of the interaction between them. In the case when repulsion forces are dominant we could hope to find Bose condensation in the exciton-gas; for attractive forces, however, the system will condense into the liquid phase. Phenomena of the Bose-condensation type[1] could then begin to develop in this liquid phase.

In the range of exciton concentrations for which the collective interactions become important, the product $n^{1/3}a_0 \sim 1$ (n is the concentration and a_0 the Bohr radius of the excitons) and difficulties arise in the theoretical study of an exciton system of such a density. In these conditions experimental investigations take on a special significance, since they enable us to trace the transition from the gas of excitons to their new state.

The first experimental investigations of a system of excitons of high density in germanium were carried out in the work[2-4], in which the occurrence of metallic properties in a system of excitons was discovered and data were given which clearly indicate the formation of an exciton condensate.

In the present paper, results are given of an investigation of recombination radiation in the exciton region of the spectrum of pure and alloyed silicon at low temperatures. The purpose of the work was to study the character of the collective effects in a system of excitons at high exciton density.

EXPERIMENTAL TECHNIQUE

In the investigation of collective effects, crystal defects can play an extremely important role; the role of the surface is especially great. Therefore, two methods were used to excite the crystal: a volume and a surface method. The scheme of the experimental setup is shown in Fig. 1. A Q-switched ruby laser was used as the light source. The frequency of the laser pulses was 3 Hz, the pulse duration was $\sim 4 \times 10^{-8}$ sec at an energy of ~0.5 J. A ray of light could either fall directly on the sample (surface excitation) or pass through a vessel of liquid nitrogen where, as a result of stimulated

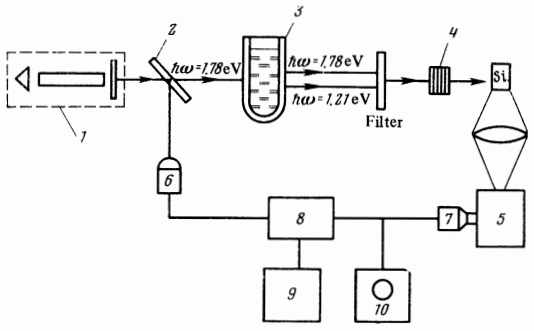

FIG. 1. Scheme of the experimental setup. 1 – Ruby laser; 2 – glass deflecting plate; 3 – Dewar flask with liquid nitrogen; 4 – attenuator for exciting light; 5 – MDR-2 monochromator; 6, 7 – photodiodes; 8 – synchronous pulse detector; 9 – ÉPP-09 automatic recorder; 10 – long-persistence oscillograph.

Raman scattering, a series of Stokes components, commensurate in intensity with the initial beam, arose[5].[1)] The second Stokes component, with quanta of energy 1.21 eV, was separated out by means of a filter; because of the small absorption coefficient in Si at low temperatures ($k \sim 1$ cm^{-1}), this component uniformly excited a large volume of the silicon crystals ($5 \times 1.5 \times 1.5$ mm).

The recombination radiation was detected by means of an MDR-2 screen monochromator and a quick response germanium photo-diode. The spectral distribution of the radiation was recorded on an automatic recorder using a synchronous pulse detector, and the kinetics of the radiation could be observed in any part of the spectrum on a long-persistence oscillograph.

The concentrations of the resulting electron-hole pairs were in the range 5×10^{16} to 1×10^{20} cm^{-3}; by volume excitation it was possible to attain concentrations of 5×10^{18} cm^{-3}. The concentration was estimated from the generation rate, since the number of incident quanta was measured and the lifetimes in the whole range of concentrations investigated was greater than the duration of a light pulse. We must note that, in our case, heating of the samples during volume excitation at high injection levels was not great. The reason is that the energy of 1.21 eV acquired by an electron in the absorption is dissipated in the crystal in two ways.

[1)] The energy in the pulse of the second Stokes component was ~0.03 J.

First the electron rapidly loses energy of the order of 0.1 eV before coupling into an exciton. This energy goes into heating of the sample. However, all the remaining store of energy is mainly converted into heat by nonradiative recombination during the exciton lifetime which is fairly long and considerably greater than the time in which detection of the peak value of the radiation pulse takes place. An estimate of the heating, in the adiabatic approximation, for an electron-hole pair concentration of 5×10^{-18} cm^{-3} and for T = 4.2°K, gives a value of ~10°K. However, in reality the heating at this temperature is considerably less; this is indicated, as will become clear below, by a comparison of spectra plotted respectively at temperatures of 4.2, 15 and 20°K at different light intensities.

EXPERIMENTAL RESULTS AND DISCUSSION

Emission spectra of silicon at various temperature and excitation intensities are shown in Fig. 2. We note the following regularities in the spectra.

1. At 77°K and a low level of excitation an exciton emission line can be seen. With increase in the injection level the emission line is displaced wholly into the long wavelength region and is broadened.

2. When the temperature is lowered, the exciton line contracts and at 20°K (and 28°K) on increase of the injection level behaves in an essentially different way. It can be seen how a new emission line is formed from the long wavelength edge of the exciton emission line, and becomes at high pumping levels a broad line that shifts to the long wavelength side with increasing injection level.

3. Of considerable interest is the behavior of the emission spectra at 15°K, which shows that the emission line of the free excitons gives rise to an emission line at 1.083 eV whose intensity increases faster with increasing pumping than does the emission intensity for the free excitons. On further increase of the injection level, the line is displaced to the short wavelength side.

4. Finally, at 4.2°K, starting with the smallest injection levels, determined by the sensitivity of the detector system, a broad line at 1.083 eV, which was earlier observed by Haynes[7] and was ascribed by him to biexciton emission, is visible. On varying the excitation level within the limits 5×10^{16} to 6×10^{17} cm^{-3}, the line is not deformed at all; however, on further increase of the excitation intensity an exciton line appears and the line at 1.083 eV is displaced into the short wavelength region, "absorbing" the exciton into itself.

A number of interesting phenomena were detected in an investigation of the kinetics of the emission. First, the exciton lifetime measured from the emission kinetics of the exciton line was ~5 μsec and was approximately 10 times greater than the de-excitation time of the emission at 1.083 eV, as is clear from Fig. 3a. Second, the type of excitation of the crystals played an important role: following surface excitation, the lifetime of the excitons fell to 1 μsec and the relaxation times for emission then differed by a factor of approximately 2.

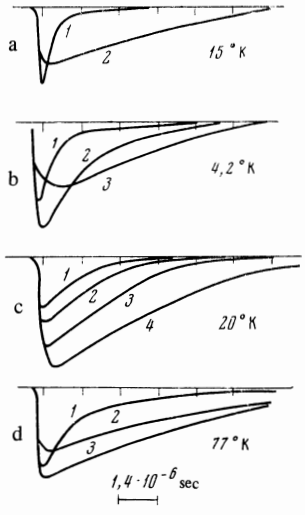

FIG. 3. (a) Curve 1 is the emission pulse at the 1.083 eV line; curve 2 is the exciton emission pulse. (b) De-excitation kinetics of the emission across the spectrum in the broad line for T = 4.2°K and $n \approx 5 \times 10^{18}$ cm^{-3} (see Fig. 2): 1) at 1.083 eV, 2) at 1.093 eV, and 3) at 1.10 eV. (c) T = 20°K, $n \approx 1 \times 10^{18}$ cm^{-3}: 1) 1.080 eV, 2) 1.090 eV, 3) 1.095 eV, and 4) 1.10 eV. (d) T = 77°K, $n \approx 8 \times 10^{18}$ cm^{-3}: 1) 1.080 eV, 2) 1.095 eV, and 3) 1.11 eV.

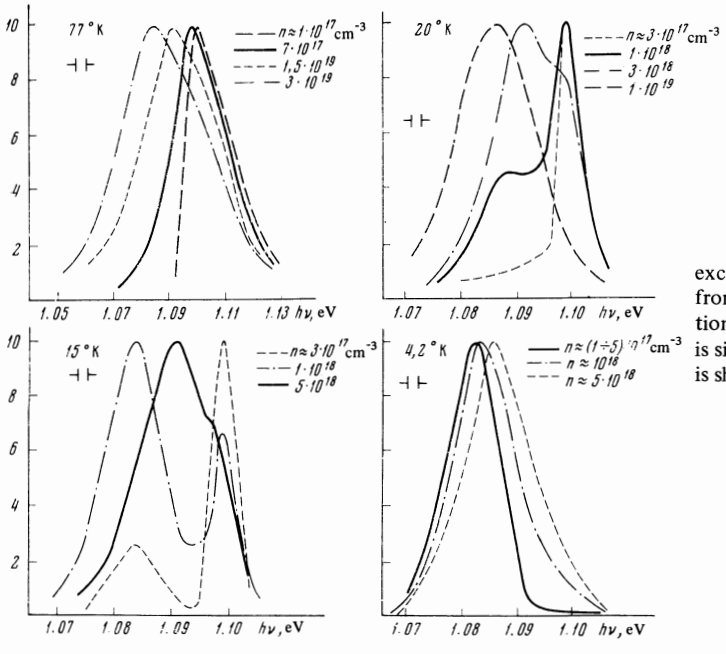

FIG. 2. Emission spectra of silicon at different temperatures and excitation intensities. The electron-hole pair concentrations, estimated from the generation rate, are indicated on the diagrams. The transformation of the emission spectra with increase of the excitation level at 28°K is similar to the transformation at 20°K. The scale of the energy spread is shown on the left of each spectrum.

We must especially emphasize that the de-excitation time in different parts of a pure exciton line was always strictly constant and did not depend on the temperature or the injection level. The emission kinetics did not vary over the line at 1.083 eV either, and the relaxation time was ~0.5 μsec.[2)] However, when the long wavelength wings appeared at higher temperatures (20 and 28°K), the emission kinetics began to vary smoothly as a function of the energy of the emitted quantum (Fig. 3c). Analogous changes in the kinetics also occurred at 77°K, when the emission line was shifted to the long wavelength side (Fig. 3d).

The shift of the exciton line to the long wavelength side with increase of the injection level at 77°K can be explained by a decrease in the energy of the excitons due to appearance of correlation in their motion, analogous to the contraction of the forbidden band observed earlier.[8] In this the shift of the long wavelength edge was found to be related to the non-equilibrium electron-hole pair concentration by the relation $\Delta E \sim n^{1/3}$. It is clear that in this case the emission decay time in the shifted exciton line will depend on the energy of the emitted quantum, since the line shift occurs in proportion to the extinction of the excitons. We note that the exciton lifetime remains constant.

At temperatures 20 and 28°K the emission kinetics also vary from point to point in the spectrum. However, the line is not shifted as a whole; a long wavelength wing grows out of it. We therefore assume that the appearance of this long wavelength wing is due to another collective effect, considered below, in the system of excitons.

The presence of the two distinct lifetimes for the exciton line and for the line at 1.083 eV implies the existence of some new entities due to the excitons. The time taken to establish equilibrium between these entities and the excitons must be large enough for observation of the two distinct lifetimes to be possible. The process of generation from the excitons and the development of the above-mentioned entities can be followed both in the emission spectra and in the dependence of the emission intensity on the pumping and the temperature.

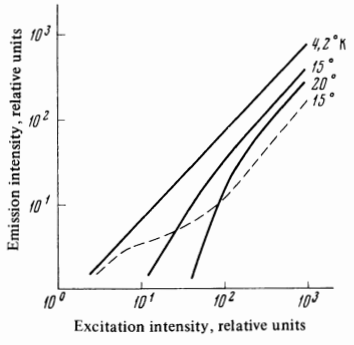

FIG. 4. Dependences of the emission intensity J on the level of excitation I. The solid curves are for recombination radiation with $h\nu$ = 1.083 eV. The dashed curve is for exciton emission.

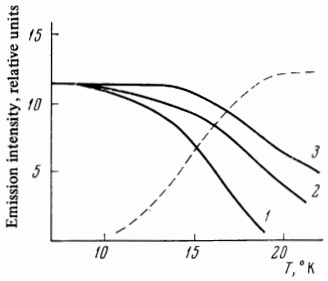

FIG. 5. Temperature dependences. The solid curves are for emission of quanta of energy $h\nu \approx 1.083$ eV at excitation levels of: 1) $n \approx 1 \times 10^{17}$ cm^{-3}, 2) $n \approx 5 \times 10^{17}$ cm^{-3}, 3) $n \approx 2 \times 10^{18}$ cm^{-3}. The dashed line is for exciton emission of quanta of energy 1.10 eV at $n \approx 5 \times 10^{17}$ cm^{-3}.

In Fig. 4, curves for the emission intensity against the pumping intensity in a region of the spectrum close to 1.083 eV are shown. It is characteristic that at low temperatures, in the pumping range investigated, there is a linear dependence. On increase of the temperature, the curves have an essentially different form, viz., there is a region of steeper linear increase and the slope in this region increases with increase in temperature. The temperature dependence of the intensity in two regions of the spectrum is shown in Fig. 5. Attention is drawn to the fact that these curves are dependent on the level of excitation.

The results given above undoubtedly indicate that at high concentrations of excitons their interaction becomes important and leads to the appearance of new entities formed from the excitons. These entities are related neither to impurities, since similar regularities were observed in both pure and alloyed material,[3)] nor to the surface, since both surface and volume excitation led to the same results.

At the present time it follows from existing theoretical ideas that interaction of excitons at low temperatures is manifested either in the formation of bi-excitons or in the appearance of a condensed exciton phase of constant density, in the form of exciton "drops." It seems to us that an attempt to explain the data obtained in the present work from the standpoint of the bi-exciton meets with considerable difficulties. Thus in the case of a bi-exciton, a quadratic dependence on the pumping level of the emission intensity would have to be observed, and the temperature quenching of the bi-exciton line would have to be independent of the number of excitons generated. A calculation of the thermal activation energy of the exciton line, which is practically identical with the energy of thermal extinction of the line at 1.083 eV, gave the value 0.015 eV, whereas the binding energy of a bi-exciton cannot be more than a third of the exciton binding energy. Moreover, the lifetimes of bi-excitons and excitons are evidently indistinguishable in order of magnitude. These considerations, and also the nature of the observed spectra, indicate that the emis-

[2)]The observed character of the emission kinetics could be used to determine the nature of the emission in broad lines. As an example, in Fig. 3b the de-excitation kinetics over the fourth spectrum at T = 4.2°K (see Fig. 2) are shown, whence it follows that within this broad line there is an exciton emission.

[3)]Silicon samples with resistivity ρ from 2500 to ~ 1 (ohm.cm)$^{-1}$ at 300°K were investigated.

sion line at 1.083 eV is not a consequence of the existence of a bi-exciton.

An attempt to explain the experimental data presented can, however, be made, by assuming that in a high-density exciton gas condensation to the liquid phase can occur at temperatures below 20°K. Evidently, at higher temperatures certain associations of excitons exist, in which there can be any number of excitons. Then the presence of the different kinetics along the long wavelength wing of the exciton spectrum implies that different association of excitons, e.g., pairs, threes, etc., are responsible for the emission at each wavelength.

These entities are "embryos" of exciton "drops" and lowering of the temperature enables an exciton "liquid" to form. We can then attempt to explain the curves shown in Figs. 4 and 5 by starting from a liquid-vapor equilibrium model. From this model it is easy to find the relation

$$N_{\text{liq}} = \bar{n}\left(1-\frac{n_0}{\bar{n}}e^{-\Delta/kT}\right)\Big/\left(1-\frac{n_0}{n}e^{-\Delta/kT}\right)$$

where N_{liq} is the number of excitons which are in the liquid phase in 1 cm^3, $\bar{n}$ is the average exciton consideration, proportional to the excitation intensity I, n_{liq} is the exciton concentration in the liquid phase, n_0 is the concentration in the "saturated vapor" of excitons and Δ is the heat of vaporization from the condensate. Since the emission intensity of the condensate $J_{liq} \sim N_{liq}$ and $\bar{n} \sim I$, we have

$$J_{\text{liq}} \sim I\left(1-\frac{\text{const}}{I}e^{-\Delta/kT}\right)\Big/\left(1-\frac{n_0}{n_{\text{liq}}}e^{-\Delta/kT}\right) \qquad (1)$$

If $n_{liq} \gg n_0 e^{-\Delta/kT}$,

$$J_{\text{liq}} \sim I\left(1-\frac{\text{const}}{I}e^{-\Delta/kT}\right) \qquad (2)$$

and the dependences shown in Figs. 4 and 5 have exactly such a character.

We must note that the time taken to establish equilibrium between the "liquid" and gaseous phases of the excitons must be extremely long,[1] and this is indeed manifested in the simultaneous presence of different lifetimes in the exciton liquid and exciton gas. However, during the laser pulse time $\sim 4 \times 10^{-8}$ sec, the formation of a strongly super-saturated vapor can evidently lead to the immediate establishment of some equilibrium situation for which expression (1) is valid.

Thus an exciton "liquid" is formed at low temperatures and with increase of the excitation level the volume of this liquid phase increases until it fills the whole sample. After this further increase in the exciton concentration will lead to increase in the "liquid" density, which evidently contributes to the change in the emission spectra when $n_{ex} \sim 1 \times 10^{18}$ cm^{-3} (see Fig. 2). If the exciton liquid is metallic[1], as soon as the sample is filled by the condensate, conductivity should appear. In fact this was observed on detection of the photoconductivity signal (Fig. 6). At low pumping levels the photo-current pulse repeated the pulse of the exciting light and the photo-current was determined by the free carriers which did not succeed in attaching themselves to an exciton. At an injected-pair concentration of 5×10^{17} cm^{-3} a sharp growth of the photo-current occurred, the kinetics of which repeated the kinetics of de-excitation in the condensate.

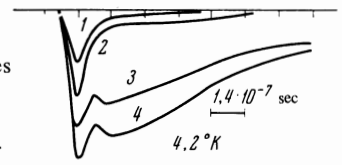

FIG. 6. Photoconductivity kinetics. The excitation intensities are: 1) $n \approx 4 \times 10^{17}$ cm^{-3}, 2) $n \approx 7 \times 10^{17}$ cm^{-3}, 3) $n \approx 1 \times 10^{18}$ cm^{-3}, and 4) $n \approx 1.5 \times 10^{18}$ cm^{-3}.

The next problem is that of the line position and linewidth of the exciton condensate and of its lifetime. The position and width of the emission line can be explained, possibly, if we assume that on annihilation of an exciton part of the energy is given up to the condensate as a whole.[4)] In this case the emission lifetime of excitons in the condensate falls by a factor of 2.5 relative to the emission lifetime of a free exciton. Such an estimate was obtained by a comparison of the emission, integrated over the spectrum, of excitons at 4.2°K (which had condensed completely) with that of the exciton gas at 20°K. As is clear from Fig. 3a, the lifetime in the condensate is decreased by a factor of 10 and, consequently, simultaneously with a new mechanism of radiative recombination in the condensate, there appear additional nonradiative decay mechanisms and the quantum yield in the condensate $\beta_k = \tau^k_{rad}/\tau^k_{nonrad} = \beta_{ex}/4$ falls.

CONCLUSION

The investigation carried out of recombination radiation of Si at high excitation levels showed that at a temperature of 77°K interaction between excitons manifests itself in the appearance of correlation in their motion, resulting in a long wavelength shift of the whole emission line. On lowering of the temperature, the exciton interaction leads to their agglomeration and to formation of associations of excitons; this is manifested by the appearance of a wing near the long wavelength edge of the exciton line, with a lifetime peculiar to these entities. And, finally, at low temperatures, the excitons agglomerate into "drops" and a broad exciton condensate emission line is formed, which for a considerable range of intensities is not deformed, indicating simply that the volume of this liquid phase is increasing.

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[4)] We note that in [7] the interaction process of two excitons was considered in the case when one exciton was annihilated and gave up part of its energy to the formation of an electron-hole pair from another exciton. In this case it is clear that the emission line must be displaced relative to the exciton line by an amount close to the binding energy of the exciton, and must be fairly broad. Apart from such a process, it is evident that annihilation of one exciton with simultaneous excitation of another exciton can occur. In exciton "drops," analogous phenomena evidently occur, with the whole drop taking part.

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