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A new emission line in highly excited ZnSe

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A new emission line from ZnSe film was observed at 10 K under high excitation. It is located at 2.774 eV, 8.6 meV below the P line. This new line grows rapidly, shifts to lower energy and gets broader with increasing excitation power. It can be interpreted as the result of inelastic scattering of a bound exciton with a free exciton, where the bound exciton recombinates radiatively transferring part of its energy to the ionization of the free exciton. The relation between the emission intensity of this line and excitation intensity was deduced based on this model. The calculated curves fit the experimental data quite well.

1. Introduction

The investigation of highly excited semiconductors has become an increasingly important field in the last twenty years. Much work has been performed on the behavior of high density carriers and excitons. It is found that when high concentrations of carriers and excitons are created, the interactions between these particles become essential and some new dynamical processes take place.

The following processes have been observed and investigated:

The inelastic scattering of two excitons, where one of them recombines radiatively, transferring part of its energy for the excitation or ionization of the other one [1].

The inelastic scattering of a free exciton and a free electron, where the exciton recombines radiatively and transfers part of its energy to the remaining electron as kinetic energy [2].

The recombination of a free exciton, with simultaneous excitation of an electron bound to a neutral donor [3].

The recombination of an exciton bound to a neutral donor, with the excitation of the donor electron [5].

The recombination of a bound exciton which transfers part of its energy to a free electron as kinetic energy [6].

In this paper, a new emission line from ZnSe film was observed at 10 K under high excitation, which is due to the inelastic scattering of a bound exciton and a free exciton.

2. Experimental setup

The excitation source is a nitrogen laser which emits pulses of 10 ns with a repetition rate of 10 Hz at 337.1 nm. The maximum of the excitation intensity I_0 is about 0.5 MW/cm^2. The luminescence was detected by a Spex 1403 spectrometer. The signals were processed through a Boxcar Averager and stored in a Datamate microcomputer.

The ZnSe film used in the experiments was prepared on GaAs (100) substrate by VPE process. The thickness of the film is about 1 μm. The sample was mounted on a cold finger of a He refrigerator, which could vary temperature from 10 to 300 K.

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3. Experimental results and discussion

At low temperature and low excitation power, we observed the emission due to free excitons, bound excitons and donor–acceptor pairs as shown in fig. 1. At medium excitation, a broad band (A band) is formed, which is attributed to the overlapping of the ordinary I_1, I_2 and I_3 lines [7]. This A band shifts to lower energies with increasing excitation and gets broader. This is because the overlapping of the A band and the well known P line, which is due to the inelastic scattering of two excitons [8]. We observed a new emission line (U line) at about 2.774 eV, 8.6 meV below the P line (see fig. 2).

This new line grows rapidly, shifts to low energy side and becomes broader with increasing excitation power. From its position and excitation dependence, the U line can be interpreted as the result of inelastic scattering of a bound exciton with a free exciton, where the bound exciton recombines radiatively, transferring a part of its energy to the ionization of the free exciton. The energy balance in this process can be expressed as the following:

bound exciton + free exciton
  → electron–hole pair + photon,

$$h\nu = E_g - 2E_x - E_b - E_K, \qquad (1)$$

where $h\nu$ is the energy of the emitted photon, E_g is the width of the band gap, E_x is the binding energy of the free exciton, E_b is the binding energy of a bound exciton to a defect, and E_K is the kinetic energy of the unbound electron–hole pair created during the collision. Neglecting the kinetic energy, we can deduce from eq. (1) that the initial rising point of the U line should be E_b lower than that of the P line. In our experiment, the U line is 8.6 meV below the P line. This value is very close to the binding energy of I_3 (8.68 meV), which is due to the recombination of the excitons bound to ionized donors. This fact indicates that the bound exciton involved in producing the U line is the exciton bound to ionized donors, which is responsible for the I_3 line.

The shift of the U line to lower energy can be explained as follows. At high excitation power, a high density of free carriers is created. The bottom of the conduction band is filled. When the scattering of the bound excitons and the free excitons takes place, the unbound electron–hole pairs created in this process must occupy higher energy states. Their kinetic energy E_K cannot be neglected anymore. Therefore a shift of the U line towards lower energy is expected.

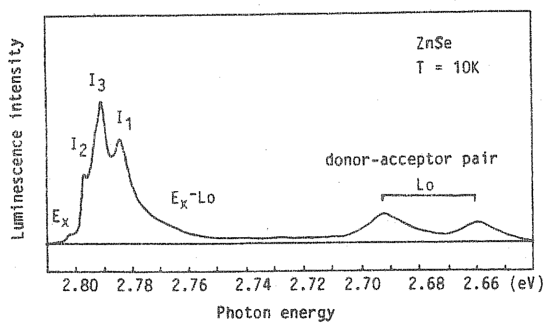

Fig. 1. Luminescence spectrum of ZnSe at low excitation and at low temperature.

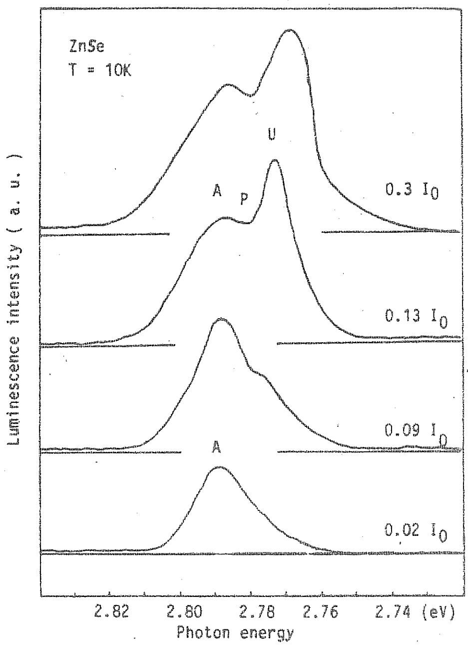

Fig. 2. Luminescence spectra of ZnSe at different excitation intensities.

From the bound-exciton–free-exciton scattering model, the relation between the emission intensity of the U line and the excitation intensity can be deduced. For simplicity, we only consider spontaneous radiation of bound excitons and bound-exciton–free-exciton scattering processes. In this case, the dynamical equation of the bound excitons can be written as

$$dn_b/dt = C_b n_x(N_b - n_b) - n_b/T - C_n n_x n_b, \quad (2)$$

where n_b is the density of bound excitons, n_x is the density of free excitons, N_b is the density of the defects to which excitons are bound, C_b is the trapping coefficient of excitons bound to the defects, C_n is the scattering coefficient of bound excitons and free excitons, T is the spontaneous radiative lifetime of bound excitons. Under dynamical equilibrium state, $dn_b/dt = 0$. The density of bound excitons is given by

$$n_b = C_b N_b n_x / [T^{-1} + (C_b + C_n) n_x]. \quad (3)$$

The emission intensity of the bound-exciton–free-exciton scattering process is then expressed as

$$I = C_n n_K n_b = C_n C_b N_b n_x^2 / \{T^{-1} + (C_b + C_n) n_x\}. \quad (4)$$

Since n_x is proportional to the excitation intensity I_e, we have

$$I = aI_e^2/(1 + bI_e), \quad (5)$$

where a and b are constants independent of I_e.

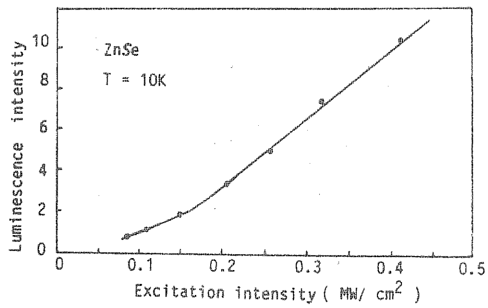

Fig. 3. Luminescence intensity of the U line as a function of the excitation intensity.

Our experimental data fit this result quite well, as shown in fig. 3.

In summary, a new emission line was observed in ZnSe film under high excitation, which is produced by the inelastic scattering of bound excitons and free excitons.

References

[1] D. Magde and H. Mahr, Phys. Rev. Lett. 24 (1970) 890.
[2] S. Iwai and S. Namba, Appl. Phys. Lett. 16 (1970) 354.
[3] J.M. Hvam, Proc. 10th Intern. Conf. Phys. Semicond., Cambridge, MA, 1970 (U.S. AEC, Springfield, 1970) p. 71.
[4] T. Goto and D.W. Langer, J. Appl. Phys. 42 (1971) 5066.
[5] C. Klingshirn, E. Ostertag and R. Levy, Solid State Commun. 15 (1974) 883.
[6] J.L. Merz, H. Kukimoto, K. Nassau and J.W. Shiever, Phys. Rev. B 6 (1972) 545.
[7] W. Maier and C. Klingshirn, Solid State Commun. 28 (1978) 13.