Multiparticle exciton complexes in semiconductors with a large exciton binding energy in (ZnO)

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A series of lines is observed at high excitation levels in the low-temperature luminescence spectra of ZnO, which are due to formation of polyexcitonic complexes. Formation of a bound electron-hole liquid based on these complexes is shown.

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A number of works published recently deal with the study of a series of narrow photoluminescence (PL) lines that occur on the longwave side of the emission lines of a bound exciton in silicon doped with group III and V elements.[1–3] The appearance of such lines is attributed to the radiative decay of multi-particle complexes that are formed in the course of consecutive binding of one, two and more excitons to impurities.[4]

It is of interest to investigate the collective properties of excitons in semiconductors with a large binding energy, for which a considerable increase is expected in the

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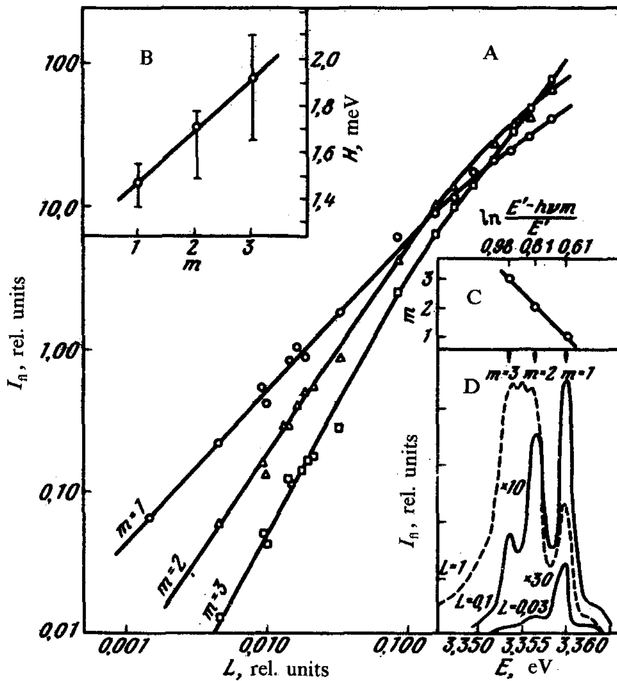

FIG. 1. A-Dependence of emission line intensity I_{fl} m-EIC on excitation intensity L; B-line half-width H of m-EIC; C-serial dependence of line position of m-EIC; D-m-EIC PL spectra at various L.

critical temperature T_c for the existence of an electron-hole liquid (EHL), in comparison with the classical semiconductors Ge and Si, since $kT_c \approx 0.1\ E_{ex}$.[5] Specific manifestation of excitons in the form of bound exciton complexes is possible in semicondutors with a large value of E_{ex}, for excitation intensities that impede the formation of EHL. In this respect a suitable material is ZnO whose exciton binding energy $E_{ex} = 59$ meV.[6]

The low-temperature edge emission in ZnO induced by a weak excitation is determined, as is known, by the radiative recombination of free and bound excitons, and in the case of high excitation intensities ($L_{exc} \geqslant 0.2$ MW/cm^2), broad bands of greater longwave radiation occur,[7,8] about whose nature a single point of view does not yet exist.

In this work we investigated the development of PL spectra of ZnO single crystals at elevated excitation levels which permitted us to study the formation of EHL comprising poly-exciton-impurity-complexes (m-EIC, where m is the number of excitons bound to a given impurity).

The edge emission was analyzed by means of a SDL-1 monochromator with a photoelectric spectrograph. The excitation source was the LGI-21 nitrogen laser operating at $\lambda = 3371$ Å and intensity of 3.4 MW/cm^2. Measurements were made at $T = 4.2$ K.

In the case of weak excitation the edge emission spectrum of ZnO is dominated by a band with $\lambda = 3690$ Å which is due to the radiative recombination of an exciton bound to a small acceptor.[7] As the excitation density L increase, two lines subse-

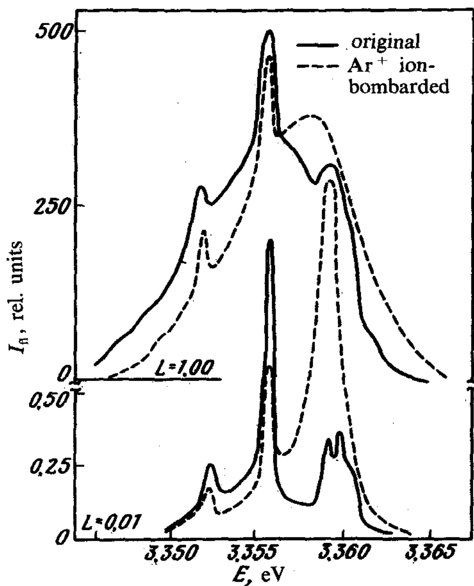

FIG. 2. PL spectra of original and Ar^+-ion-bombarded ZnO sample.

quently appear with $\lambda = 3694$ Å and $\lambda = 3697$ Å which, as L increases, form a broad PL band (Fig. 1D).

Lines that are similar in structure were first observed in Si,[1] where their polyexciton nature was established. The existence of m-EIC in direct-zone semiconductors was proposed in Refs. 9 and 10.

The observed emission lines from ZnO exhibit the following characteristic features of m-EIC emission lines (Fig. 1): (1) they are located on the longwave side of the emission lines of a bound exciton ($m = 1$); (2) as the pumping level increases longer wavelength lines subsequently appear ($m = 2$, $m = 3$); (3) the half-width of the H lines is below 1.5–2 meV; (4) a noticeable increase of H is observed with respect to increased m; (5) the line intensity variously depends on the pumping intensity $I \sim L^n$; in the case of lines with $m = 1$, the function is linear, and with $m = 2$ and $m = 3$ it is ultralinear; moreover, the higher the m, the steeper the slope of the function ($n \geqslant 2$). During the radiative decay of a complex ($m \rightarrow m-1$) the observable photon energy consists of an energy difference between the initial and final states; $h\nu_m = E_g - E_{ex} - E_m = h\nu_{ex} - E_m$, where E_m is the exciton binding energy in an m-complex. In our experiments, the following values of E_m were obtained: 16.8, 20.4, 23.1 meV (for $m = 1,2,3$, respectively). We found that the observed lines, as is also the case in Si,[2] may be described by a weak power function of the type $E_m = E'(1 - Ae^{-\alpha m})$, where $E' = 37.2$; $A = e^{0.45}$; $\alpha = 0.18$ (Fig. 1C), or $E_m \sim (m + 0.5)^{1/2}$,[11] as opposed to $1/m^2$ which was predicted by the hydrogen-like model. The value of E' with respect to physical content is determined by the formation of a bound EHL-phase in an m-EIC: $h\nu_{EHL} = h\nu_{ex} - E'$.

Based on the statistics of formation and decay of m-EIC we may qualitatively predict the nature of the function $I(L)$ for each line:

$$n_m = (C\tau_{\rm EIC})^m N_d e^{-C\tau_{\rm EIC} n_{ex}} \frac{n_{ex}^m}{m!} \sim \frac{L^m}{m!} \quad (\text{ since } n_{ex} \approx L(CN_d + \tau_{ex}^{-1})).$$

For $m = 1,2,3...$ at low intensities ($C\tau_{\rm EIC} n_{ex} \ll 1$) linear, quadratic, etc dependences are predicted respectively, which qualitatively corresponds to the experiment (Fig. 1A).

The shell model[4] predicts the appearance of m-EIC only for semiconductors with degenerate zones. In connection with this, the presence of transitions with the participation of sufficiently strongly dispersed excited states of the impurity centers ($\Delta E \approx 3$ meV) should be assumed for single-valley direct-zone semiconductors, a fact that is natural for centers that are not too small ($E_{tc} \approx 80$ meV).[11] Thus, the existence of m-EIC is possible in ZnO at least for the case when three excitons are bound with an impurity center.

As was stated above, when the excitation levels are sufficiently high ($L \gg 1$ MW/cm^2) the emission lines $\lambda = 3694$ Å and $\lambda = 3697$ Å are transformed into a broad line, the so-called M-band.[8] The ocurrence of the latter can be explained in terms of the biexciton model. In our case, the free biexciton model appears to be improbable since the experimentally observed shape of the PL lines fails to correspond to those calculated theoretically (see, e.g., Ref. 12). On the other hand, a similar M-band in CdS[9,10] is explained by the radiative decay of m-EIC that serve as condensation centers of the electron-hole plasma in EHL. Our results confirm the latter model.

A substantial effect on the PL spectrum of ZnO derives from the ion-plasma (Ar^+) surface processing which, evidently, gives rise to significant mechanical fields, semi-metallic islets (due to changes in the stoichiometry of a semiconductor), and simple surface defects. The latter may serve as centers of binding single- and poly-EIC. Changes in the PL spectrum which occur as a result of argon-ion bombardment ($E = 1$ keV, $D = 10^{15}$ ion/cm^2) are shown in Fig. 2 for small and large ($L = 1$ MW/cm^2) pumping levels; they attest to the formation of m-EIC on a ZnO surface, which under conditions of high center density appear in the form of a broad emission band.

Thus, low-temperature ($T = 4.2$ K) photo-luminescence spectra of ZnO single crystals yield new emission bands that occur with increasing excitation density. The proof of the poly-excitonic nature of these bands was shown. The analysis leads us to conclude that the formation of a bound electron-hole liquid can be attributed to poly-exciton impurity complexes.

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