Picosecond kinetics of emission by surface excitons in ZnO

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(Submitted 13 July 1989)
Pis'ma Zh. Eksp. Teor. Fiz. **50**, No. 3, 113–116 (10 August 1989)

It is shown, for the first time, that a substantial fraction of the exciton luminescence of ZnO crystals is due to excitons trapped by surface centers. It is suggested that the anomalously short lifetimes (~ 60 ps) observed for the surface excitons are a consequence of Auger processes.

During the excitation of semiconductors by photons with an energy above the band gap E_g, free charge carriers and excitons are produced. They rapidly become trapped at various defects. Because of the high absorption coefficient for photons of this energy, most of the excitons and carriers are formed in a narrow surface layer of the semiconductor. It might therefore be suggested that surface defects play an important role in the trapping of free excitations. In the present letter we report the first demonstration that the photoluminescence of ZnO single crystals excited at liquid-helium temperatures by single-photon interband excitation essentially always contains an intense emission band associated with trapped surface excitons.

The luminescence of ZnO was excited at a temperature of 4 K by the second harmonic of a quasi-cw, synchronously pumped dye laser. The excitation wavelength was 310 nm, the pulse length was 3 ps at a repetition frequency of 82 MHz, and the average power ranged up to 2 mW. The spectral resolution and temporal resolution were 2 Å and 3–5 ps simultaneously.[1] Steady-state emission spectra were recorded by a photon-counting method.

Figure 1 shows the part of the photoluminescence spectrum which was studied. The insets at the top show the time evolution of the various components of this spectrum. Line I_7 is an emission of excitons bound at neutral donors in the interior.[2] The rise and decay times of this emission, which characterize the formation and decay of the exciton complex, are 100 ± 20 and 350 ± 50 ps, respectively.[3] Line I_{10} is also an emission of trapped bulk excitons, with equal rise and decay times, 700 ± 50 ps.

The photoluminescence spectra of all of the samples we studied reveal a relatively broad emission band, which we designate as I^s. This band is characterized by a much more rapid kinetics: a rise time of 18 ± 5 ps and a decay time of 60 ± 15 ps. This band has a characteristic long-wavelength tail out to ~ 372 nm, with the same time evolution. This tail is particularly obvious if the spectrum is plotted in logarithmic scale (Fig. 2). The spectral position of I^s, its high relative intensity, and the presence of a long-wavelength tail suggest that in this case, as in the case of CdS (Refs. 4 and 5), we are dealing with trapped surface excitons.

To find proof of the surface origin of the I^s band, we measured the photoluminescence spectrum immediately after the crystal was cleaved in liquid helium, so that we

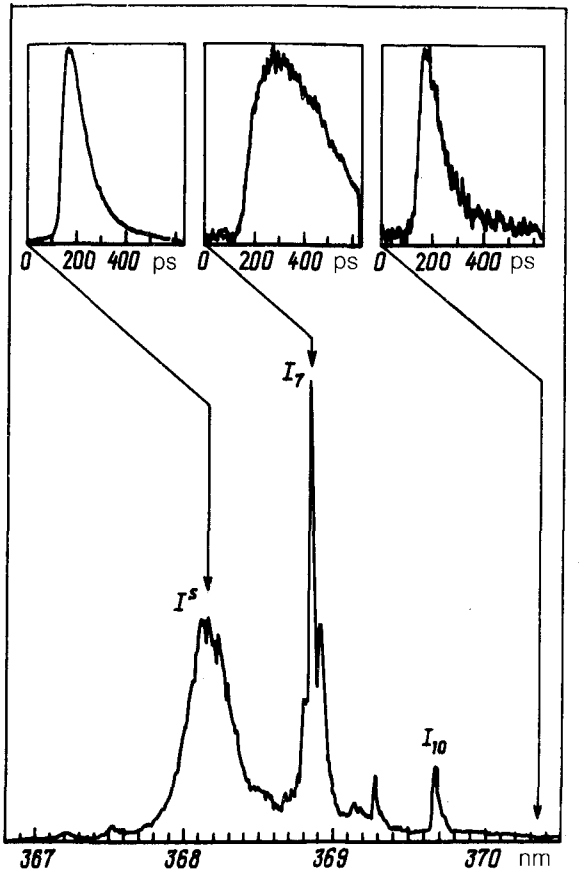

FIG. 1.

would be dealing with a clean surface. In this case the I^s band was not observed (spectrum 1 in Fig. 3). After the sample was exposed to air for a day and then cooled, I^s reappeared in the spectrum (spectrum 2). Note also the substantial decrease in the intensity of I^s after a preliminary exposure of the surface to photons with $h\nu > E_g$.

These results show that adsorbed gas molecules or atoms are apparently part of the centers near the surface which trap excitons. This circumstance would explain the absence of I^s in the case of the freshly cleaved face, and it would also explain the effect of illumination, which would reduce the density of surface centers by virtue of desorption.

The asymmetric shape of the lines, with an elongated long-wavelength tail, is characteristic of the emission of excitons trapped at neutral centers in the interior in the case in which the distance between centers becomes comparable to the Bohr radii of the excitons.[6–8] In this case the tail may be a consequence of either a Stark energy shift of a trapped exciton in the electric field of ionized (neutralized) impurities near-

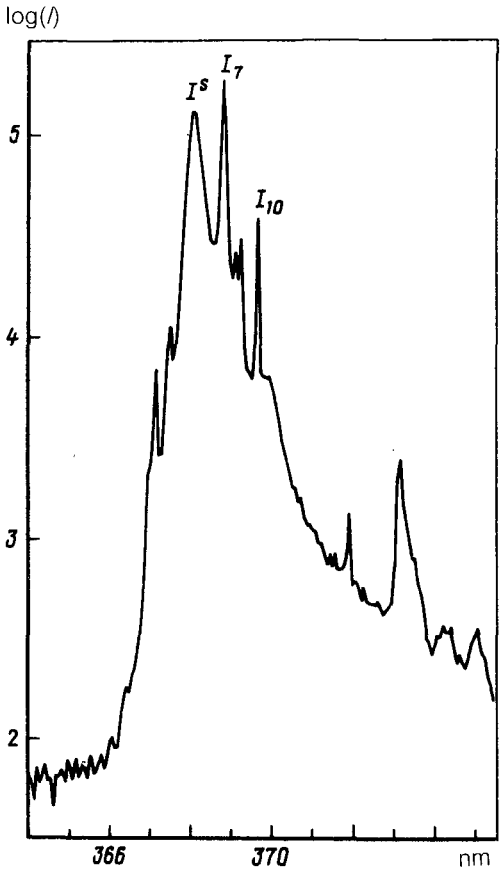

FIG. 2.

est the center[6,9] or an interaction of a trapped exciton with other neutral impurities in the immediate vicinity.[8,10] The observed features of the I^s band can be understood if it is assumed that this band is a consequence of excitons which are trapped at neutral surface centers of an acceptor nature, whose concentration corresponds to the conditions for the appearance of the long-wavelength tail described above. Such surface centers could arise during the trapping of photoexcited holes by negatively charged surface states (the predominant type of surface states of ZnO in the absence of illumination).

The observed decay time of the surface excitons (τ) is much shorter than the radiative lifetimes characteristic of bound excitons. This shortening of τ, as well as the appearance of a long-wavelength tail, could be explained in terms of the effect of the electric field of charged surface states. In this case we would naturally expect a significant decrease in τ in the long-wavelength I^s tail as a result of a field-induced dissociation in the strong fields responsible for the energy shift of a trapped exciton. However, we did not observe this effect experimentally.

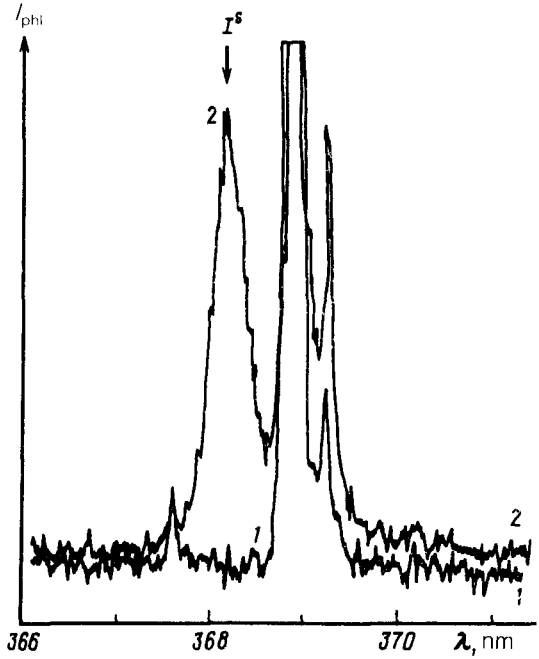

FIG. 3.

The measured value of τ agrees with estimates characterizing the Auger decay of excited states of excitons trapped at neutral centers in the interior ($\sim 10^{-10}$ s; Ref. 11). We believe that Auger decay also determines the kinetics of the decay of I^r. With respect to the ground states of trapped excitons in the interior, excitons trapped at surface centers are excited states, since as a center moves out of the interior to the surface, the wave function of the trapped exciton should convert from a $1s$ function to a $2p$ function. As a result of this effect, and also as a result of other possible effects of the surface, the prohibitions against Auger decay which are imposed by the symmetry and which are characteristic of trapped excitons in the interior may be lifted for surface excitons.[11] The identical values of τ over the I^s tail might be explained, on the basis of this model, by the fact that an increase in the exciton trapping energy due to the increasing proximity of other centers is not accompanied by a substantial change in the Bohr radii of the carrier motion (around one of the centers), which determine the corresponding overlap integrals.

Calculations by Agekyan *et al.*,[8] show that the probability for radiative transitions also remains generally the same in the case of a pronounced increase in the trapping of excitons due to the effects of neighboring centers. The anomalously small value of τ, however, makes, in our view, Auger decay the process most likely to be responsible for the decay of I^r.

Further research is required to definitively establish the mechanisms for the emission and kinetics of surface excitons. We might note that the mechanism proposed

here for the Auger decay of surface excitons is extremely effective and might be a candidate for the role of the mechanism responsible for surface recombination, which has not yet been studied adequately.

We wish to thank V. A. Kharchenko for useful discussions.

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Translated by Dave Parsons