Complex spectrum of exciton-impurity complexes in imperfect crystals of tin dioxide

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Luminescence spectra of free and localized excitons in SnO_2 were obtained. A phonon-free spectrum has a complex structure whose properties indicate that the excitons are localized on the interacting defects. A significant variation of the energy of the longitudinal optical phonons, which interact with the localized excitons, was detected.

PACS numbers: 71.35. + z, 71.55.Ht, 71.50. + t, 78.55.Hx

1. Industrial application of SnO_2 is determined by its transparency in the range from 0.4 μm to the near infrared region and by its ability to vary the conductivity in a wide range by alloying and annealing. It was recently discovered[1] that at $T \geqslant 4$ K the SnO_2: Sb bolometers are better than the best germanium bolometers in the far infrared region. This increased the interest in the spectroscopy of imperfect SnO_2 crystals. The absorption spectra of free excitons (FE) and of the exciton-impurity complexes (EIC) in SnO_2 were investigated by Nagasawa and Shionoya[2] and Agekyan[3]; however, de Murcia *et al.*,[4] for example, observed in the luminescence only an impurity emission because of the low quality of the crystals.

2. In this study we obtained exciton absorption and luminescence spectra of crystals alloyed by the elements of the groups III and V by the thermal diffusion method. It was found that the produced EIC spectrum is almost independent of the chemical impurity which determines the main function of the intrinsic defects. The impurity
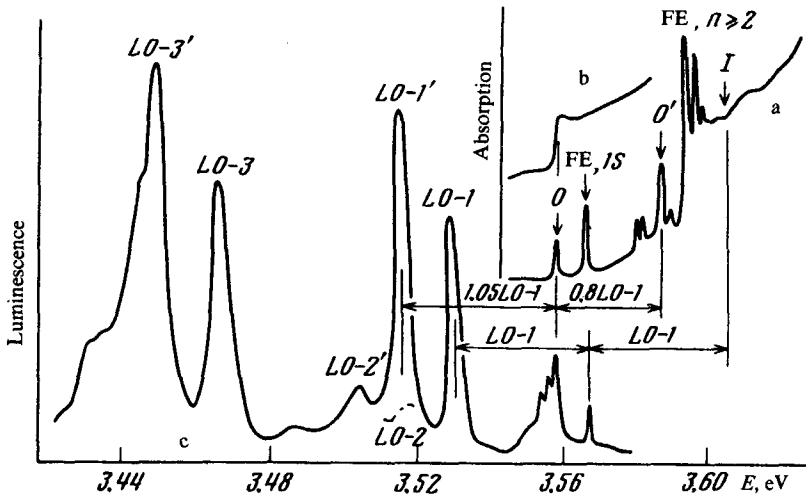
FIG. 1. spectra of absorption (a and b) and photoluminescence (c) of SnO$_2$ crystals with defects at $T = 4$ K: LO-1, 2, 3 and LO-1', 2', 3' represent the emission of free excitons and exciton-impurity complexes with the involvement of longitudinal phonons with energies of 295, 370, and 770 cm^{-1} and symmetry $^2\Gamma_5$.

probably initiates the formation of oxygen vacancies, since an analogous spectrum is produced also after a lengthy deoxidization in vacuum. Two most common EIC spectra, which have a different structure of the excited states, can correspond to the nonequivalent positions of oxygen in the SnO$_2$ lattice. The second possibility is the localization of excitons in the complex center consisting of an impurity and an intrinsic defect. In this case the EIC spectrum is produced as a result of reduction due to formation of a defect near the atom of the uncontrolled impurity. At a high concentration of the defects the absorption spectrum begins with a step whose boundary is the O line-ground state of EIC (Fig. 1). The appearance of a step may indicate the beginning of a migration of excitons along the defects, which produces phonon-free states with a nonvanishing momentum in the absorption spectrum of imperfect crystals.

3. The spectrum of exciton luminescence of SnO$_2$, which is excited by a focused nitrogen laser beam, consists of phonon-free FE and EIC lines and their phonon repetitions with LO phonons (Fig. 1). The energy of the LO-1 phonon (295 cm^{-1}) in the FE radiation coincides with the phonon energy in the indirect exciton absorption I (Fig. 1), so that the FE spectra have a mirror symmetry. The parameters of SnO$_2$, on the whole, are favorable for formation of the exciton-phonon bound states.[5] In the case of $1S$ FE the absorption maximum of the bound state with LO-1, which fits exactly the absorption edge, broadens and becomes almost unobservable. The sharp edge of the indirect transition 1 indicates, however, that the FE-LO-1 phonon bound state plays a minor role. An intensive O' line, whose energy state is rigidly bound to the O line, stands out from the group of lines of the EIC absorption adjacent to the FE with $n \geqslant 2$, whereas the location of the other lines-excited EIC states-varies as a function of the defects. The O' line is a phonon satellite of O, since there are no other manifestations of coupling of the localized excitons (LE) with the LO-1 phonon in the
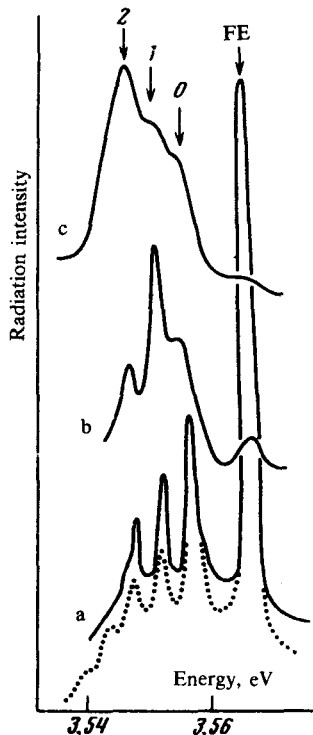
FIG. 2. Phonon-free emission of EIC (0,1,2) and of a free exciton (FE) in SnO$_2$. The concentration increases from "a" to "c". $T = 4$ K. The dotted line represents spectrum "a" at $T = 2$ K.

absorption and, according to the luminescence data, this bond is strong. The energy spacing OO' is only 0.8 of the LO-1 phonon energy of the SnO$_2$ lattice, whereas in the luminescence the distance from the O line to its phonon repetition is equal to 1.05 of the LO-1 energy. A strong violation of the mirror symmetry of the EIC spectrum is attributable to the formation of the LE-phonon bound state: the transition from FE to LE turns to zero the parameter of the Hermanson's theory,[5] which depends on the mass of the carriers, and this increases the bound state.

4. The structure of the phonon-free radiation of EIC, which consists of four lines and a long-wave wing, is an important property of SnO$_2$ luminescence. In more perfect crystals, in which a strong FE radiation is observed at $T = 4$ K, the most intensive line of the phonon-free EIC lines is the short-wave-resonance line with the O absorption line. The EIC lines 1 and 2 increase in intensity as a result of increasing the concentration of the defects and FE dampens (Fig. 2). The heating of the crystal at $T = 4$ K greatly intensifies the O line (Fig. 3), whereas the phonon repetitions of LE, especially those with the LO-3 phonon, are weakened. A nontrivial monotonic luminescence damping of FE occurs as a result of heating of the crystal. The phonon-free line of the 1S FE weakens faster than its phonon repetitions probably because the temperature of a fraction of excitons with small momenta decreases.

5. The complexity of the phonon-free EIC spectrum may be the result of the appearance of multiexciton impurity complexes (MEIC) (Ref. 6) or the localization of
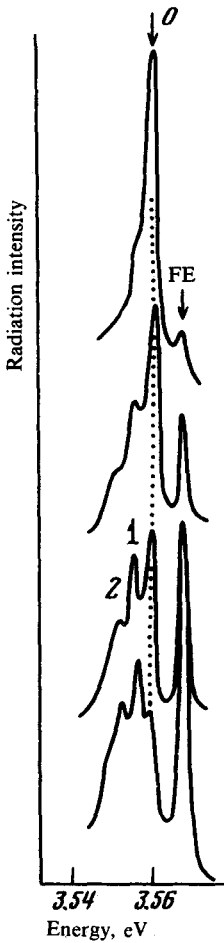
FIG. 3. Intensification of the resonance line O as a result of heating SnO_2 at $T = 4$ K. The temperature increases from bottom to top.

excitons in the interaction defects. The dependence of the intensities of the lines 0, 1, and 2 on the concentration of the defect (Fig. 2) favors the second possibility-formation of the exciton-aggregate complexes (EAC). The intensification of the O line and degradation of the lines 1 and 2 as a result of heating (Fig. 3) is attributed to weakening of the interaction of the defects, which increases the concentration of the LE in the isolated centers. The structure of the phonon-free EIC spectrum is pronounced in the LO-3' repetition and is hardly noticeable in LO-1', which causes a sharper temperature quenching of the LO-3' repetition. An analogous group of lines observed in heavily alloyed silicon[7] was identified as the MEIC spectrum. In contrast to pure silicon, Saker[7] probably observed EAC: this makes it possible to explain the absence of an O line even in case of a weak excitation and its occurence in the luminescence with increasing T. We can assume that at high concentration of the defects the formation of EAC due to localization of excitons, which migrate along the individual defects, plays an important role. The localized excitons in the interacting centers must have a

greater oscillator strength than those in the isolated centers, analogous to the well-known case[8] for LE as compared to FE.

To completely explain EIL spectrum in SnO_2, we must account for the absence of appreciable resonance absorption in the emission lines 1 and 2 at any concentration of the defects: only the narrow intensive O line corresponds in absorption to the spectrum in Fig. 2b; the stage with a sharp long-wave O boundary corresponds to the spectrum in Fig. 2c.

The high concentration of the defects, which inhibits the diffusion of excitons from the excited bulk, increases the actual excitation level and can strengthen the concentration dependence of the SnO_2 radiation spectrum.

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