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Optical properties of ZnO:Al epilayers: Observation of room-temperature many-body absorption-edge singularity

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We have studied the evolution of optical absorption spectra in eight samples of n type ZnO:Al as a function of excess electron concentration up to $6.7 \times 10^{20} \text{ cm}^{-3}$ at 300 K. The spectral assignment is examined by taking the many-body effect due to the presence of high-density electron gas into account. We propose that absorption-edge singularity induced by many-body Coulomb effect is observed for the concentration up to $4.8 \times 10^{19} \text{ cm}^{-3}$ at room temperature. Such edge singularity has been so far observed at temperatures less than 50 K in other semiconductors. The strong Coulomb interaction between electrons and holes inherent to ZnO may be related to the persistence of the edge singularity up to room-temperature.

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The optical properties of wide bandgap semiconductors are currently subject of tremendous investigations, in response to the industrial demand for optoelectronic devices that could operate at short wavelengths. Zinc oxide is an interesting wurtzitic semiconductor. The large exciton binding energy¹ (R_0) of ZnO (60 meV) allows one to observe the optically pumped laser action of excitonic origin even at room temperature (RT).²⁻⁴

Heavily-doped n -ZnO is also important from both fundamental and applied points of view. Structures based on such material can be used potentially for several kinds of semiconductor devices such as resonant-tunneling devices and Bragg reflectors for surface-emitting lasers. For these kinds of applications it is highly desirable to have knowledge of its optical properties.

Here we wish to point out the importance of the many-body Coulomb effect for the correct assignment of optical spectra in n type ZnO. Interband optical absorption spectra from undoped, direct-gap semiconductors are characterized by two thresholds:⁵ a discrete excitonic feature, and a continuum edge shifted up in energy from the bound state by R_0 . In contrast, in the presence of a high density of free carriers the spectra exhibit only a single threshold that typically appears as a steplike edge enhanced at the threshold. The enhancement in the vicinity of the Fermi level [the Fermi-edge singularity (FES)] is observed in modulation-doped semiconductor heterostructures and results from the many-body response of the mobile electrons to the photoexcited valence hole.⁶⁻¹⁰

The problem about the evolution between these two extremes, as a function of the excess electron density (n_s), has been studied theoretically and experimentally for metals and two-dimensional semiconductors. The obtained knowledge is summarized as follows;¹¹⁻¹⁶ (i) many-body Coulomb effect modifies the simple excitonic spectra to the form of power-law singularity above a certain critical density of n_s . (ii)

Absorption threshold energy is located in the vicinity of the resonance energy of the unscreened excitons even when the n_s is considerably above this critical density. As n_s increases, the sharp excitonic feature should broaden asymmetrically to higher energies: a fast rise at the low-energy side and a slow fall at high energies. The critical density is significantly lower than the Mott critical density (n_M) above which the degeneracy of the conduction band takes place. It is reported to be $n_M \gg 10^{19} \text{ cm}^{-3}$ in ZnO.¹⁷ The injection of a photocreated hole into an electron gas creates a bound state below the conduction band edge. This kind of knowledge enlightened the authors. It lead to reexamination of spectral assignment for n type ZnO films along this line although this material has a long research history.¹⁷⁻²⁰

In this Rapid Communication, we present RT absorption spectra that allow us to quantify the evolution of the threshold line shape as a function of the density of the excess electron (n_s). We conclude that, in some of our n type ZnO:Al samples, the line shape showed a form of power-law singularity which is consistent with the model of many-body absorption-edge singularity. The RT observation should be noted because such edge singularity has been so far observed at temperatures less than 50 K in semiconductors.^{6,14} Because it is reported that the nonlinearity associated with the many-body or Fermi-edge singularity is larger than that for exciton resonance,^{21,22} its RT observation must open numerous possibilities for optical nonlinear devices.

In the final part, we comment on the other researchers' interpretations^{20,23,24} for their optical spectra taken for similar ZnO samples.

The 150-nm-thick ZnO epitaxial layers doped with Al have been grown on lattice-matched ScAlMgO₄(0001) substrates by laser-molecular-beam epitaxy.²⁵ We measured optical absorption spectra in these samples at 300 K. It should be noted that only a single excitonic peak is observed in the spectra taken at RT for undoped, high-quality samples.^{1,26}

TABLE I. Sample specification for the eight n -ZnO samples. Nominal aluminum concentration of n_{Al} , carrier concentration of n_s , absorption threshold energy of E_1 , and the deduced and calculated coupling parameters of α and α_{cal} . Because the concentration (n_s) of the S01 is below our measurement limit, n_s is estimated from n_{Al} .

Sample	n_{Al} (10^{18} cm^{-3})	n_s (10^{18} cm^{-3})	E_1 (eV)	α	α_{cal}
S01	9.63	5–10	3.295	0.13	
S02	33.4	19	3.322	0.13	0.373
S03	35.9	48	3.324	0.14	0.314
S04	44.1	59			0.302
S05	76.5	210			0.235
S06	85.5	270			0.222
S07	99.5	380			0.207
S08	142	670			0.183

because the A and B excitons cannot be resolved well spectrally. The contribution of C excitons are very weak because of the c axis orientation. The concentrations n_s were evaluated by Hall-effect measurements (Van-de-Pauw configuration) at RT. The sample specifications are compiled in Table I.

Dashed lines of Fig. 1 show the n_s dependence of experimental values of the absorption coefficient corresponding to the three n type samples of S01, S02, and S03. All these spectra have the asymmetrical shape: a fast rise at the low energy side and a slow fall at high energies. Peak energies

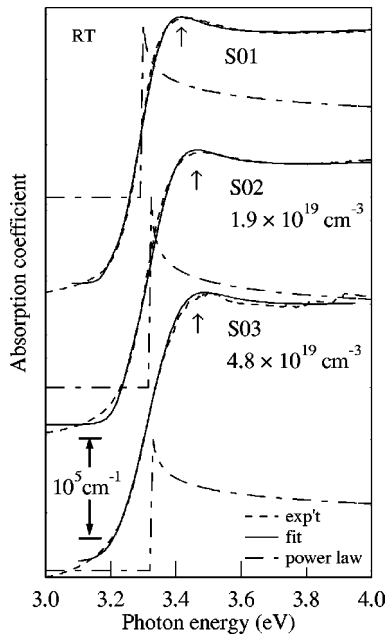


FIG. 1. The dashed and solid lines are the experimental and fitted values, respectively, of the absorption coefficient $A(E)$ for the samples of S01, S02, and S03 taken at RT. Dash-dotted lines indicate the power-law singularity functions used in the fitting. Upward arrows show the peak energy positions. Vertical bar indicates the scale corresponding to the coefficient of 10^5 cm^{-1} .

are 3.41 eV for S01, 3.45 eV for S02, and 3.48 eV for S03, which are shown by upward arrows. These spectra could not be well reproduced by the following four models: (i) Elliott's model describing a simple Wannier exciton picture,^{5,27} (ii) Tanguy's model,²⁸ (iii) Lucovsky's model,²⁹ and (iv) the model related to the Burstein-Moss (BM) effect.³⁰ The second one gives the analytical expression of absorption coefficient of the Wannier excitons, which includes the screening effect of Coulomb potential. The screening is induced when the large carrier density is present. Many-body effect was, however, not taken into account in this theory. The third one is associated with the optical transition from the valence band to the donor impurity band. It should be noted that the coefficient of the relevant absorption processes is typically several orders of magnitude smaller than that observed in Fig. 1. The line-shape deduced by the last model reflects the Fermi distribution of carriers. In addition, possibility of the Fabry-Perot interference also has to be definitely ruled out, because correction for the reflection loss at the sample surface has been certainly made. Therefore, we attempted to adopt the earlier-mentioned model of many-body edge singularity.

The line shapes of the experimentally observed singularities can be fitted using the following form. Following Mahan,³¹ the absorbance edge should exhibit a power-law divergence of the form:

$$A(E) = A_0(E) \left[\frac{\zeta_0}{E - E_1} \right]^\alpha, \quad (1)$$

where E is photon energy, ζ_0 is a cutoff energy, E_1 the threshold energy where the optical absorption sets in. The coupling parameter α provides a phenomenological measure of the strength of the singularities.^{12–14,32}

The factor $A_0(E)$ in Eq. (1) contains the simple Wannier excitonic result. Because the sample thickness is larger than the excitonic Bohr radius or diameter of this material (18 or 36 Å), three-dimensional version should be used. For the sake of simplicity, Goni's expression was adopted in which the effect of lifetime broadening was taken into account.²⁷ This is chosen:

$$A_0(E) = \text{const} \left[\frac{R_0 \Gamma_0}{(E_0 - R_0 - E)^2 + \Gamma_0^2} + \int_{-\infty}^{\infty} \frac{\Theta(E' - E_0)}{1 - \exp[-2\pi z_1(E')]} \frac{\Gamma_0 dE'}{(E - E')^2 + \Gamma_0^2} \right], \quad (2)$$

where E_0 is the value of a fundamental band gap in the excitonic picture, Γ_0 is the broadening parameter, $z_1(E) = \{R_0/(E - E_0)\}^{1/2}$, R_0 is the exciton binding (Rydberg) energy, $\Theta(E)$ is step function. To account for the inhomogeneity broadening we performed a numerical convolution of Eq. (1) with a Gaussian distribution.³³ The half-width of Gaussian distribution of Γ_{Gauss} account for the inhomogeneity broadening.

The above formalism [Eq. (1)] was used to explain our absorption spectra. The results are shown in Fig. 1 with the solid lines. The deduced fitting parameters are shown in

Table I. The peak positions in the dash-dotted lines correspond to the deduced values of E_1 . The fitted result is in surprisingly good agreement with the experimental data over a sufficiently wide energy region. This probably indicates that the many-body edge singularity was observed even at RT in these samples by virtue of the strong Coulomb interaction inherent to this ZnO system. Note that generally such spectral singularity has been observed in bulk crystals³³ or modulation-doped superlattices composed of narrow-gap semiconductors^{6,14} at temperatures less than 50 K. The width Γ_{Gauss} is typically 85–115 meV. The choice of broadening Γ_0 's influenced the fitting results sensitively at energies more than 3.75 eV. Therefore, they could be determined easily to be 40–120 meV for the displayed three samples. In contrast, determination of band gap energy (E_0) was rather difficult. It is much less influenced by the choice of E_0 between 3.27 and 3.33 eV. The deduced E_0 is lower than the literature values (3.37–3.38 eV).¹ This corresponds to the bandgap reduction, which is likely to occur with the doping of donors. This is induced by the electron-electron interaction^{30,33} and the so-called bandgap tailing effect.¹⁹

The deduced threshold energies, E_1 (cf. Table I), are close to the excitonic resonance energy of undoped samples (3.31–3.32 eV).¹ In addition, its blueshift is less drastic than that of the well-known BM effect (the shift is proportional to $n_s^{2/3}$). Thus, these E_1 's may correspond to those of the bound electronic states predicted in theories of Combescot and Nozières, and Hawrylak.^{12–15} These theories insist that the injection of a photocreated hole into an electron gas always creates a bound state below the conduction band edge, no matter how high n_s is. This bound state is recognized as being composed of the electron from the Fermi sea and the photocreated hole. The transition energy of this occupied state smoothly evolves from that of the exciton states of the extremely low n_s spectrum. This is consistent with the experimentally-observed n_s dependence of the threshold energy (E_1). It is unnecessary to consider the doubly occupied state. The charged exciton which is the corresponding concept of low-density limit has been observed only in quantum wells in which the low-density excess electrons are introduced in the barrier layers.

It was found from previous research that the coupling α are the monotonically increasing functions of Coulomb interaction strength and of hole localization strength. The larger Coulomb interaction makes it easier to observe the many-body edge singularity. According to Mahan,³¹ an approximation for α is given by:

$$\alpha_{cal} = \left(\frac{R_{se}}{6} \right) \ln \left(1 + \frac{6}{R_{se}} \right). \quad (3)$$

R_{se} is a dimensionless density parameter which depends on the electron concentration n_s and the excitonic Bohr radius of the (dielectric) semiconductor, a_B :

$$R_{se} = (3/4 \pi n_s)^{1/3} / a_B. \quad (4)$$

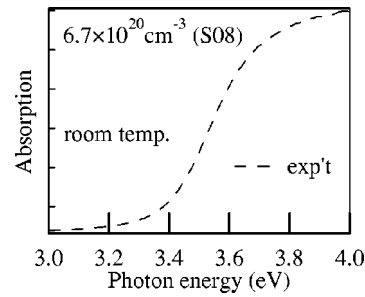


FIG. 2. Dashed line is the experimental values of the absorption coefficient $A(E)$ for the sample S08 with $n_s = 6.7 \times 10^{20} \text{ cm}^{-3}$.

Evidently R_{se} is the ratio of the radius of the volume which contains one unit charge e of the Fermi sea to the excitonic Bohr radius (neglecting the spin degeneracy).

The calculated α_{cal} 's for ZnO were compiled in Table I and are larger than those of other narrow-gap semiconductors.^{14,33} The larger α_{cal} of ZnO may result in the RT observation of edge singularity.

Generally, the strong hole localization has been accepted as a criterion in which the FES appears.^{6,13,33} The hole localization, in this case, probably arises because of microscopic fluctuation in the aluminum concentration.

The α 's estimated through the fitting are smaller than the calculated values (α_{cal}). The reason for the smaller α is not clear, but considered to be the very efficient impurity scattering. This can be speculated from the very small mobility (typically $3\text{--}8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) of our samples. Impurity scattering may obscure the observation of the edge singularity and reduce the coupling parameters.³³ It should be also noted that the recent theoretical works^{13,14} reported the smaller values of α_{cal} .

The dashed line in Fig. 2 is the absorption spectra in a n -ZnO:Al sample with $n_s = 6.7 \times 10^{20} \text{ cm}^{-3}$. This n_s is significantly larger than n_M . One cannot see the spectral singularity structure here probably because of the decreased α [see Eq. (3) and Table I] and the increased broadening parameter (Γ_{Gauss}). The coupling parameter α_{cal} is a monotonically decreasing function of carrier density. This means that the FES limit could not be observed experimentally at RT. The absorption line-shapes of the five most heavily doped samples ($n \geq 5.9 \times 10^{19} \text{ cm}^{-3}$) reflect the Fermi distribution of carriers. In other words, these spectra (S04–08) could be interpreted in the framework of BM effect.³⁰ The fitting results were shown in Ref. 34.

It is considered that the use of the modulation doping is more promising for optoelectronic application, because this is expected to overcome the problem regarding the high- n_s -induced disappearance of FES.

We comment on the other researchers' interpretations^{20,23,24} for their optical spectra taken for nominally-undoped (but surely n type) ZnO, or n type ZnO films doped with group-III elements. New (but physically unrealistic) parametrizations have been obtained through the fitting to their experimental data. For example, the broadening parameter of free electron-hole pairs is negligibly small compared with that of excitons (the energy-dependent- Γ_0 was adopted).^{23,24} In another study, it was insisted that the donor-

doping induces the one-order-of-magnitude enhancement in the R_0 .²⁰ In our speculation, even in their cases, the better agreement between fitting and experimental data would be obtained when the above-mentioned model [Eq. (1)] was employed.

In summary, we have studied the evolution of optical absorption spectra in eight samples of n type ZnO:Al as a function of n_s up to $6.7 \times 10^{20} \text{ cm}^{-3}$ at 300 K. Some of these spectra differ from those of the simple excitonic picture and are characterized by: (i) asymmetric line shape of absorption threshold, and (ii) continuous evolution of the threshold energy from the excitonic limit with the increase of n_s . The spectral assignment was reexamined by taking the presence of high-density electron gas into account and in the framework similar to the FES.^{13–16} We propose that absorption-edge singularity induced by many-body Coulomb effect was

observed in the samples with $n_s \leq 4.8 \times 10^{19} \text{ cm}^{-3}$ at RT. Such edge singularity has been so far observed at temperatures less than 50 K in other semiconductors.¹⁴ The strong Coulomb interaction between electrons and holes inherent to ZnO may be related to the persistence of the edge singularity up to room temperature.¹ This work successfully supplied one more interesting phenomenon realizable at RT that renders ZnO among the most fascinating semiconductors of the near future.

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