Optical properties of ZnO aggregates in KBr matrix

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Abstract. Zinc oxide nanocrystals were prepared, using Czochralski method of growth, in KBr matrix during pulling. Good evidences can prove that the quantum confinement effect is the special quality for this nanosystem. As an indication of quantum confinement effect, excellent emissions from band edge have been observed in optical absorption spectra and on selective PL ones. CL spectrum exhibits several levels in band gap allotted to different types of impurities in matrix and within ZnO aggregates.

Keywords: quantum confinement effect, zinc oxide, nanocrystals, exciton.

1. Introduction

Semiconductor nanocrystallites are of great interest because of their unique optical properties and potential applications for optoelectronics [1,2]. In recent years, a great deal of work has been carried out focusing a special emphasis on the nanocomposites of quantum dots embedded in some wide-band-gap dielectric matrices, for the advantage of stabilizing dots and being adapted to device manufacturing process [3,4]. One can list manufacturing nanoparticles encapsulated in carbon nanocage structures used as cluster protection, nano-ball bearings, nano-optical–magnetic devices, catalyst and biotechnology [5–7]. Insulating sheets such as alkali halide matrixes are required for optical devices since these hosts are optically isotropic and transparent in a large visible field. Over the past decade, the optical properties of ZnO QDs have been extensively investigated [8,9]. It can be used in field-emission displays with development of the fat panel display industry and various optical devices, and the luminescence efficiency of ZnO is required to be substantially improved.

In this paper we report optical studies of ZnO QDs embedded in KBr matrix. Samples are obtained using Czochralski method. During pulling process, with translating and rotating rates equal to 1cm/houre and one lap by minute, respectively, we dope the melted solution of KBr, in a temperature around 900°C, with a commercial ZnO fine powder. It is important to note that the property of this powder seems to be sufficiently good. A PL spectrum done on this ZnO powder proves this assertion. Then, samples in the form of plate discs with thickness averaging 1mm are subjects for optical absorption measurements at ambient temperature, photoluminescence at the temperature of liquid helium and finally cathodoluminescncece studies. CL experiments have been done at an ambient temperature, where a fine electronic beam are used having an energy equal to 5eV. The ambient temperature is only done because this device is, unfortunately, not adapted to low temperatures ones.

2. Optical absorption measurements

Absorption measurements were carried out using a Shimadzu spectrophotometer at ambient temperature. Fig. 1 exhibits a series of picks corresponding to a various size distributions. The first transition corresponding to the absorption edge is located at 4.3816 eV, with a displacement of 1.07eV compared to the absorption edge of bulk ZnO crystal which is about 3.307eV.

Such displacements were observed in crystallites of ZnO produced by oxidation of zinc metal where authors measured displacement of 0.1 eV for a diameter variation of 610 Å to 200 Å [10]. In addition, C.L.Yang and al.[11] measured the absorption of ZnO crystallites about 31 Å average size and they find a threshold absorption around 3.974 eV. A blue shift averaging 0.667 eV compared to the bulk crystal.

We evaluate the mean size of crystallites by applying the Kayanuma formula [12] defined in the case of a strong confinement by:
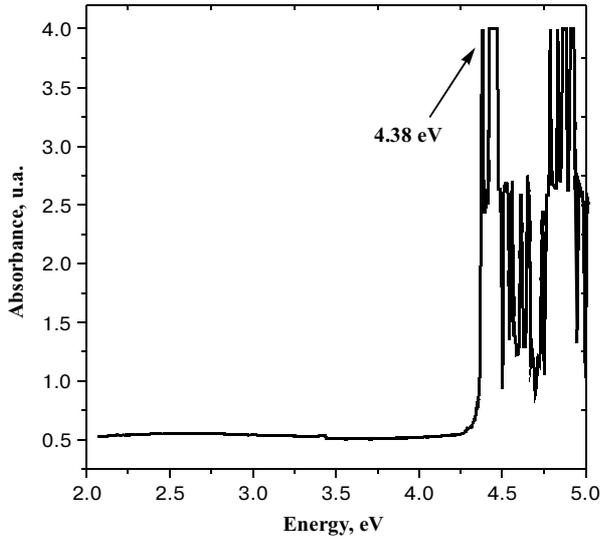
Fig. 1. Absorption spectra of ZnO crystallites embedded in KBr matrix in ambient temperature.
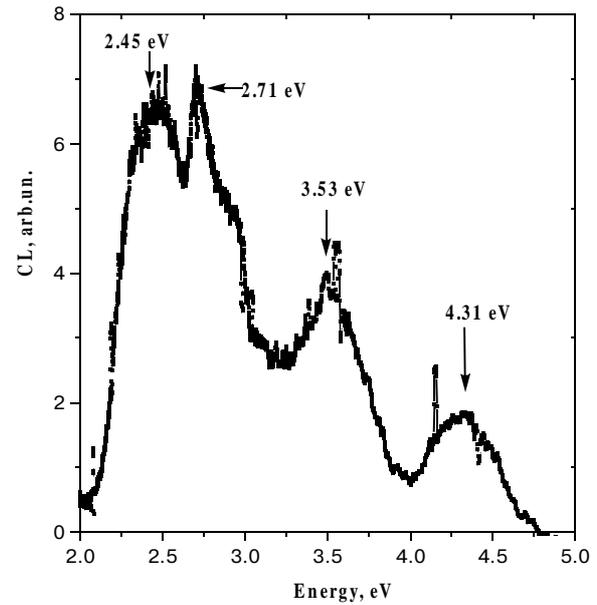
Fig. 2. Cathodoluminescence spectra of ZnO particles embedded in KBr matrix at ambient temperature.

$$E_{ex} = E_g + \frac{\hbar^2 \pi^2}{2\mu R^2} - \frac{1.786}{\varepsilon R} - 0.248 \frac{\mu e^4}{2\hbar^2 \varepsilon^2}$$

Where E_g is the band gap of bulk semiconductor; R is the mean radius of QDs; ε is the dielectric constant;

$$\mu = \frac{m_e * m_h}{m_e + m_h}$$ reduced mass of the electron (m_e) and the hole (m_h); e is the electronic charge and $\hbar$ is the Planck constant, devided by 2π.

With $m_h = 0.59 m_e$, $e = 7.8$ [13] and the band gap value is estimated to be equal to 3.307 eV in ambient temperature [14], we find a mean size of ZnO particles equal to 26Å.

3. Cathodoluminescence spectra

In the UV part, the spectra presents a very solved band, whose center is located at 4.312 eV bellow 69 meV from edge of absorption of the sample which is positioned at 4.381 eV. This shift value corresponds to the energy of phonon replica in crystallites which equal, in bulk ZnO, to 72 meV. This prevalence of the transitions coupled to optical phonons is observed in the spectrum of photoluminescence of ZnO crystallites in KBr matrix [15]. Based on arguments mentioned above, this band corresponds to the recombination of excitons, free or/and bound slightly on impurities with phonon replica. The broadening of this band is due to several factors; coupling with phonons and the size distribution. In addition, the interaction of the acoustic phonons with exciton increase with the reduction of the crystallites size whereas the interaction with optical phonons remains almost insensitive with the reduction of the size [16,17] due to the relaxation of

rules selection in crystallites caused by the deterioration of the translation symmetry required in bulk crystal.

The appearance of emission band of free excitons is a very rare experimental fact particularly in crystallites within strong confinement due to the fact that for small crystallite dimensions, the surface-volume ratio being large and induce strong densities of levels in the band gap. Consequently, it induces radiative and non-radiative recombinations via these levels with densities depending on crystallite-matrix interface quality and the chemical nature of elements which can diffuse in crystallite through its surface.

On the weak side of energies, appears a second band relatively strongly intense, located at 3.53 eV. It is allotted to recombinations via levels in the gap introduced by surface defects or by impurities which would have diffused from matrix within ZnO crystallites. One also observes a third less intense band located at 3.1147 eV as a tail. This contribution is identified in KBr as emission levels of Cu$^+$ ions in KBr matrix [18].

Fig. 2 exhibits also a fourth band, strong intense, with the position of 2,769 eV. This peak is due to the recombinations via the levels introduced by the impurities Cu into ZnO. Into the green area of the spectrum, one observes a broad and very intense band whose center locates at 2.420 eV. This green band is observed around 3.4 eV in bulk ZnO crystals worked out by vapor phase deposition [19].

4. Photoluminescence spectra

To consolidate cathodoluminescence results, we carried out a photoluminescence characterization at temperature of 1.6 K with a power of 10 mW, using the excitation
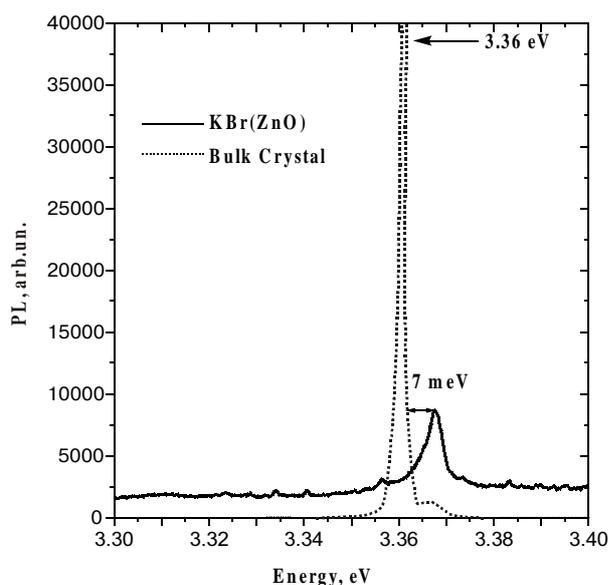
Fig. 3. Photoluminescence spectra of both bulk and nanosized ZnO at the temperature of liquid helium.

of laser based Argon plasma emitting a wavelength of 351nm. This measurement is likely used to confirm the presence of various size distributions of crystallites by a selective excitation.

The spectrum obtained is represented on fig. 3. It exhibits a peak of intensity of width at half height equal to 5 meV roughly. This effect demonstrates the low disparity of the size distribution of crystallites. The band is located at 3.367 eV. Y. Harada and al.[15] obtained an emission band of ZnO crystallites averaging 200 Å size in a matrix similar to the position 3.363 eV. Referring to this paper, we allot this band to bound excitons emission related to defects located on the surface of crystallites. Compared with the value of the energy position of the emission band of bulk crystal (3.360), we find a shift towards great energies of 7 meV, due probably to quantum confinement effect. This weak shift involves the situation of weak confinement defined within the framework of the approximation of the effective mass. The mean size of crystallites corresponds to 157 Å, with the effective masses of electron and hole equal to $0.28m_0$ and $0.59m_0$ respectively [20].

The difference between QDs sizes measured by optical and PL measurements can be explained by the fact that PL one is a selective experiments where a photonic beam, at a precise energy was used contrary to optical ones. Then in PL measurements only a part of size distribution will response to excitation and all particles or aggregates having a size less then this mean size of distribution will not appears leading, consequently to an apparent mean radius greatest.

5. Conclusions

In conclusion, with Czochralskɪ growth device, we can manufacture ZnO nanocrystals embedded in alkali-halide matrix with different size distributions. Optical results confirm the presence of theses particles within host matrix with several size distributions. Our results can be described in terms of the quantum confinement effect. In both PL and optical absorption spectrum, we observe transitions involving excitonic and impurities levels inside bandgap. Therefore, this surface defaults can improve the emission property of ZnO, which is very important for the developing high quality nano-devices.

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