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TIME-RESOLVED PHOTOLUMINESCENCE OF SINTERED ZnO CERAMICS*

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The time-resolved photoluminescence (TRPL) of sintered ZnO ceramics was measured at low temperatures. A broad luminescence band was observed in the visible region. The TRPL experiment shows that photoluminescence decay behaviour can be depicted as $t^{-n(r)}$. The decay rate $n(r)$ and lifetime are wavelength dependent, and the former varies exponentially with wavelength. The power-lowering behaviour of the luminescence intensity indicates that the luminescence band originates from the recombination of donor–acceptor pairs.

Keywords: time-resolved photoluminescence, sintered ZnO ceramics
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I. INTRODUCTION

Zinc oxide is a versatile material that can be applied in varistors, anti-reflection coatings, transparent electrodes in solar cells, gas sensors, and surface acoustic wave devices.[1–6] This material has a high efficiency as a low-voltage phosphor and has been used in vacuum fluorescent displays (VFDs) and field emission displays (FEDs). Because FEDs are one of the promising candidates for flat panel displays, it has become important recently. Inspired by the application of ZnO, many studies have appeared on the nature of the visible luminescence from ZnO.

There are several visible and infrared emission bands that are related to the presence of impurities and defects, as reviewed in Ref.[7]. Several groups have studied the green luminescence band of ZnO.[8–14] Dijken *et al.*[12] studied the steady-state and time-resolved luminescence on suspensions of nanocrystalline ZnO particles with different sizes and assumed that the visible emission is due to the transition of an electron from a level close to the conduction band edge to a deeply trapped hole in the bulk. Vanheusden *et al.*[8,9] studied the green photoluminescence (PL) band of ZnO phosphor powders and proposed that the defect centre responsible for the green PL is the singly-ionized oxygen vacancy. Kamat *et al.*[13] studied the emission decay of ZnO colloids at room temperature and fitted the decay curves to three exponential components. This suggests that different radiative or nonradiative decay tunnels exist. Despite much research on the nature of the visible luminescence from ZnO, the mechanism behind the visible luminescence has been very difficult to establish. There are still different opinions about the origin of the visible luminescence centre and mechanism.

Time-resolved photoluminescence (TRPL) provides an effective nondestructive technique for studying the dynamics of impurities and lattice defects in semiconductors.[14–18] In the present work, the TRPL of sintered ZnO ceramics is investigated in the visible region at low temperatures in order to study the luminescence behaviour of sintered ZnO ceramics. A broad PL band was found in the visible region and its decay behaviour can be depicted as $t^{-n(r)}$. The decay rate $n(r)$ decreases exponentially with wavelengths. The lifetime is wavelength dependent and obviously lengthened from short to long wavelengths. The power-lowering behaviour of luminescence intensity indicates that the green band originates from the recombination of donor–acceptor (D–A) pairs.

II. EXPERIMENTAL DETAILS

The ceramic samples used in this work were produced with analytic pure zinc oxide powder (99.5%), without any artificial additives. Firstly, pure ZnO powder was grinded and pressed into slices. These slices were placed in an electric furnace and sintered in air for 2h at 1350°C. Then the furnace was cooled to room temperature. After all these procedures the size of the slices decreases obviously. The as-sintered specimen of ZnO shows an approximately white colour.

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The TRPL measurement was performed using a streak camera in conjunction with a quarter metre spectrometer employing a 150 lines/mm grating. A second harmonic generation (SHG) of a mode-locked Ti:sapphire laser synchronously pumped by a laser diode (LD) was used for excitation. The excitation wavelength was 365nm with a pulse duration of 1.5ps. The average power of the output laser was 0.5mW with a repetition rate 18kHz and was focused into a spot of 0.1mm diameter on the surface. The ZnO ceramic specimen was mounted in the cold finger of a helium-cycled cryostat where the temperature was cooled to 10K for PL measurement. The energy density on the sample was $30\mu J/cm^2$ per pulse. Light emitted from the specimen was collected and focused into the entrance slit of the spectrometer, the wavelength ranging from 400 to 700nm. The time resolution and spectral resolution of this system were about 10ps and 0.3nm, respectively.

Ⅲ. RESULTS AND DISCUSSION

A broad visible band is observed in our experiment, which is mostly similar to the early results.[8−14] Figure 1 shows the broad PL band of the sintered ZnO ceramics with different time delays at 10K. Compared with the TRPL of colloidal ZnO suspension in ethanol at room temperature in Ref.[13] an obvious difference exists. In Ref.[13] an exciton emission band appears around 400nm and overlaps severely with the visible band around 410 nm. However, exciton emission does not appear in our measurement range and the intensity of the visible band is very weak until 450nm. No overlap appears between the exciton and visible emissions. This is likely for larger grains in sintered ZnO and longer wavelength excitation. It is evident that the lifetime of this band is of the order of hundreds of nanoseconds, and the central wavelengths will shift toward the long wavelength side with a time delay.

PL decay curves of five different wavelengths, 450, 490, 545, 600 and 670nm, in the green band are shown in Fig.2. All of these are similar to each other except the 450nm curve with a very steep and brief initial decay. The decay curves at different wavelengths all display an approximately straight line in the bilogarithmic coordinates in the time region from 50–500ns investigated. In other words, the PL intensity of the green band can be depicted approximately by t^{-n} in the period. It is obvious that the decay rate n of shorter wavelengths is faster than that of longer wavelengths.

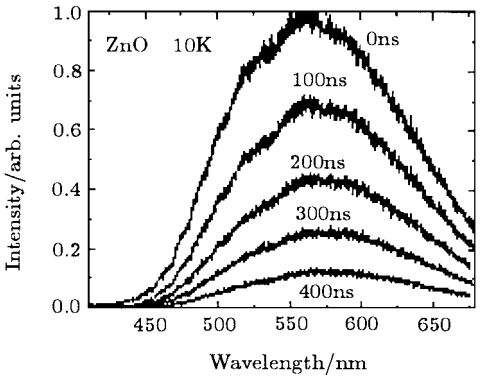


Fig.1. The PL spectra with different time delays at 10K. The central wavelengths shift toward the long wavelength with increasing time delay.

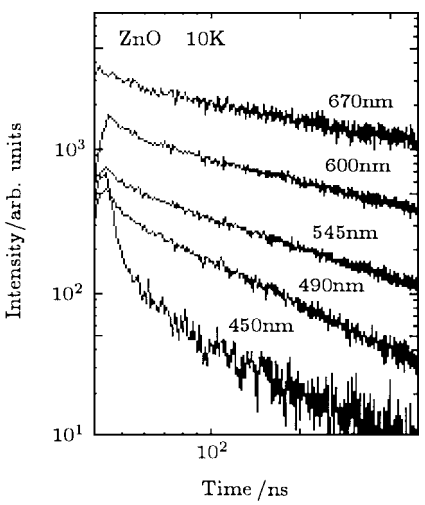


Fig.2. The PL decay curves of five different wavelengths in the green band. They can be depicted as t^{-n} in the period.

In the luminescence band of D–A pair recombination, because of the Coulombic energy of interaction between the electron–hole pairs, its emission energy can be expressed by [19,20]

$$E(r) = E_g - (E_D + E_A) + e^2/\varepsilon r, \qquad (1)$$

where E_g is the band-gap energy, and E_D and E_A are the donor and acceptor binding energies, respectively. The symbol r is the D–A separation, and ε is the low-frequency dielectric constant. Therefore, a smaller D–A separation r corresponds to a higher Coulombic energy, and consequently the emission appears in the short wavelength region of the band.

The decay rate $n(r)$ dependence of wavelengths in the green band is shown in Fig.3. $n(r)$ is larger in the shorter wavelength region than in the longer wavelength. This figure shows an obvious exponential relation. The lifetime is defined as the time interval of decay from the maximum to $1/e$ of the maximum,

and its wavelength dependence is shown in Fig.3. It is evident that a longer lifetime appears at the longer wavelength.

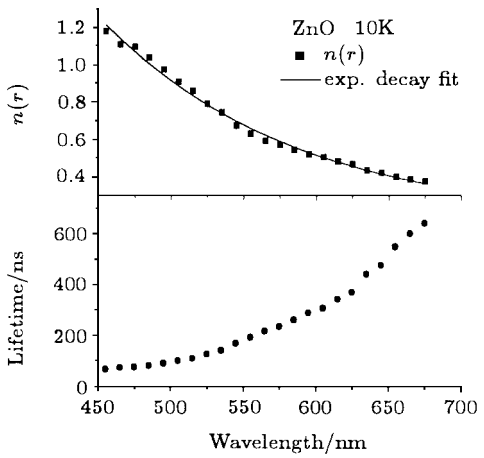


Fig.3. The decay rate $n(r)$ and lifetime dependence of wavelength in the green band. The solid line is an exponential fitting.

At low temperatures the radiative decay is dominant and the total decay rate originates mainly from radiative recombination of D–A pairs. The decay rate $n(r)$, corresponding to recombination of D–A pairs, increases with decreasing distance between electron–hole pairs. The close pairs with a small r emit faster than the distant pairs and the corresponding emission appears at shorter wavelengths. The distribution of such excited states at various trapping sites in ZnO ceramics is responsible for the emission with different lifetimes.

A higher recombination rate will appear for shorter wavelengths, which results in a faster decay rate in short wavelength region. The central wavelengths shift toward long wavelengths with a delayed time because the longer wavelength emission has a slower decay rate, and its radiative contribution to the overall emission increases with increasing time. The PL intensity dependence of the wavelength in this band can be written as

$$I(t) = I_0 t^{-n(r)}. \tag{2}$$

This power-lowering behaviour of the luminescent intensity dependence of time is well known for the tunnelling recombination between electrons and holes trapped in impurity or defect centres, i.e. D–A pairs,[18] likely a conduction electron and a deeply trapped hole at an oxygen vacancy ($V_{\ddot{O}}$).[12] This is the direct evidence of D–A pair luminescence for the green band origin.

IV. CONCLUSIONS

The TRPL of sintered ZnO ceramics has been investigated in the visible region at low temperatures. A broad PL band is found in the visible region and its decay behaviour can be expressed as $t^{-n(r)}$. The decay rate $n(r)$ varies exponentially with wavelength. The power-lowering behaviour of the luminescence intensity indicates clearly that the green band originates from the recombination of D–A pairs.

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