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Measurement of the time-resolved spectrum of photoelectrons from ZnS:Mn, Cu luminescent material

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Abstract

The process of decay of photoelectrons in the conduction band of ZnS:Mn, Cu luminescent materials after excitation with a short-pulse laser has been investigated in this paper by means of measurements made using the microwave absorption dielectric spectrum detection technique. Exponential decay processes were observed for the electrons in the conduction band and the shallow-trapped electrons; the lifetimes of the electrons were found to be 1177 and 1703 ns, respectively. The processes of decay of the luminescence from ZnS:Mn, Cu were investigated and exponential decay processes were found for blue Cu⁺, green Cu⁺ and Mn²⁺ luminescent centres with lifetimes of the excited state of 139, 140 and 680 μ s, respectively.

1. Introduction

As one of the most important luminescent materials, ZnS:Mn, Cu had been widely used in colour television, radar, oscilloscope displays, photoluminescence materials and electroluminescence materials [1–6]. ZnS is also a kind of semiconducting material with a band with an energy gap of 3.54 eV. ZnS-type semiconducting luminescence devices and semiconducting quantum well devices have been made using its good semiconducting properties [7, 8]. ZnS nanomaterials have received a great deal of attention in recent years because of their curious luminescent characteristics [9–20].

Upon doping ZnS with an activator such as Cu⁺, Ag⁺, the inner structure of the energy levels in ZnS is changed, with the formation of acceptor levels and various recombination centres. Mn²⁺ is frequently used as an activator of ZnS material and the separate luminescent centres of Mn²⁺ was found in ZnS material upon the addition of Mn²⁺; orange light was observed with a wavelength of 585 nm. The electrons transfer from the valence band to the

conduction band with the absorption of ‘foreign’ energy; the formation of free electrons and hole carriers was observed. Luminescent centres luminesce under excitation or following recombination due to electrons in the conduction band, when the electrons in the conduction band meet the luminescent centres.

Donor level and shallow electron traps were obtained by doping with Br^- , Cl^- , Al^{3+} and there were S^{2-} holes in ZnS. The electrons trapped by traps, including shallow and deep electron traps, are called trapped electrons in the process of migration in the conduction band. A temporary trapping effect was observed for electrons in shallow traps and the trapped electrons can escape back to the conduction band and become free electrons, while the deep electron traps can capture the electrons permanently. As reported by Zhu *et al* [21], a shallow electron trap can be formed in ZnS by doping with Br^- .

Many studies on time-resolved spectra of luminescent materials are reported in the literature; the lifetime of the excited state of a luminescent centre is thoroughly understood [22–24]. However, we have found very little research into the relaxation process in the conduction band—the process of movement of photocarriers. This process directly reflects the migration efficiency, range of freedom, collision cross-section and trapping capture for electrons in the conduction band. Therefore, the investigation of the process of decay of electrons in the conduction band is very important to the study of luminescence [25–28].

Contactless detection of photocarriers can be carried out using the microwave absorption dielectric spectrum detection technique, with high precision and low interference. This method was applied to measure the changes undergone by carriers in the imaging process for silver halide (AgX).

There are very few direct measurement techniques that can be used to establish the movement of carriers in powders and polycrystals. The microwave absorption dielectric spectrum detection technique is suitable for investigating dynamic processes undergone by photocarriers of semiconducting nanomaterials, powder luminescent materials, micropowder and nanocrystal materials and multicrystal membrane materials. Investigation of the kinetic decay process for free photoelectrons and shallow-trapped electrons is helpful in achieving an understanding of the kinetic mechanism of luminescence and the energy level structure for luminescent material or other semiconducting crystal materials; also, it can provide a scientific basis for the improvement of the luminescence efficiency of semiconducting materials.

2. The measurement principle

Figure 1 is a diagram showing the measurement principle. The sample was set in the middle of the microwave cavity. The microwave frequency is 35 GHz, the power is 143 mW, the quality coefficient $Q = 186$, the bandwidth is 1 GHz and the time resolution is 1–2 ns. The valence band electrons were excited by irradiation with short-pulse laser; a large number of free electrons and shallow-trapped electrons were obtained and this resulted in a change of the susceptibility tensor. One modulates the length of microwave cavity such that a harmonic state is achieved. The microwave field intensity is processed using a PSD (phase-sensitive wave detector). The signal is divided into microwave absorptive and reflective components and they are recorded by an oscilloscope and sent to a computer for further analysis. According to [28–30],

$$P_n = q_n x_n N_n / V \quad (1)$$

where P_n is the susceptibility tensor and N_n is the number of carriers in the sample of volume V ; q_n and x_n are the charge and displacement of carrier number n , respectively. The change

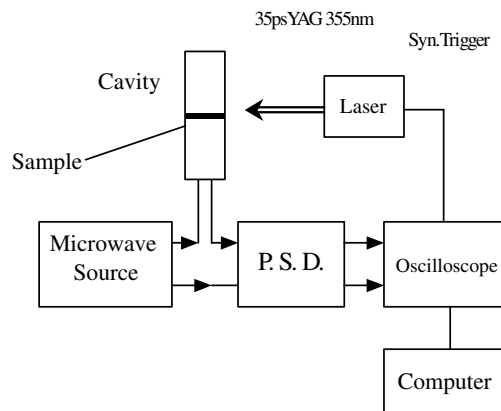


Figure 1. A diagram of the experimental apparatus.

in the imaginary part of P_n can be considered as the microwave power:

$$\Delta P = V_s E_s^2 e \mu \Delta n \quad (2)$$

where E_s is microwave electric field, V_s is the sample volume, μ is the carrier mobility, e is the electric charge and Δn is the number density of photocarriers. The reflection signal in the microwave cavity, from calculation, is

$$U' = U Q_0^2 \delta^2 - 0.5 U f Q_0 \varepsilon'' + i U Q_0 \delta - 0.5 i U f Q_0 \varepsilon' \quad (3)$$

where U is the incident microwave, U' is the reflected microwave, $\delta = (\omega_{res} - \omega)/\omega$ is the change in the resonant vibration frequency, ω_{res} is the resonant vibration frequency (35 GHz), ω is the resonant vibration frequency when the sample is added, $\varepsilon = \varepsilon' + i\varepsilon''$ is the complex dielectric constant, Q_0 is the quality factor of the resonant vibration cavity and f is the filling factor.

The first and third terms in the above equation are direct current parts and the stationary state signals without illumination; the second term ($0.5 U f Q_0 \varepsilon''$) is in direct proportion to the density of free electrons; the fourth term ($0.5 U f Q_0 \varepsilon'$) is in direct proportion to the density of electrons in shallow electron traps. The two signals were measured separately using a phase-sensitive detection system. The observed absorption signals are approximately in direct proportion to the density of free electrons while the dispersion signals are in direct proportion to the density of shallow-trapped electrons.

The samples were placed in the window of the spectrometer and irradiated with the YAG pulsed laser. The samples' emission spectra were measured; the intensities at wavelengths of 450, 520 and 585 nm were measured respectively. These intensities were recorded with an oscilloscope and sent to a computer for further analysis.

3. Experimental details

3.1. Apparatus

The YAG laser (France Quantel Company) was used at a pulse width of 35 ps and at a wavelength of 355 nm. A digital fluorescence oscilloscope (Tek.TDS3052, 500 MHz) was used throughout. The measurements were conducted at 25 °C.

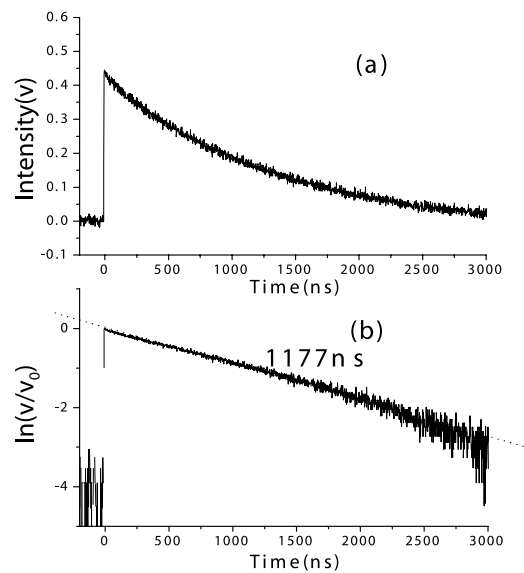


Figure 2. The decay curve for the free photoelectrons of ZnS:Mn, Cu.

3.2. Sample preparation

Certain amounts of cupric salt (high purity, 0.1 wt% ZnS) and manganous salt (high purity) were doped into ZnS (spectroscopic purity, 0.2 wt% ZnS) and the materials were stirred to achieve homogeneity, with the addition of an appropriate amount of water. After heating in an oven to dry at 120 °C and ball grinding for 24 h, the ground materials were put into a quartz tube and sintered for 1 h at 850–950 °C under protective gas ($\text{NH}_4\text{Br} + \text{S}$). The materials were taken out and the Cu_xS on the surface of the materials was washed off using a basic solution. Then the materials were washed to neutrality with high-purity water and dried at 120 °C for measurement.

4. Results and discussion

4.1. The process of decay of the free photoelectrons and weakly bound electrons

The decay curves for the free photoelectrons of ZnS:Mn, Cu is shown in figure 2(a). The results show that the number of free electrons in the conduction band showed exponential attenuation; the number of free electrons in the conduction band is given by

$$n \propto e^{-t/\tau} \quad (4)$$

where τ (the lifetime of electrons in the conduction band) is, in figure 2(b), 1177 ns.

Figure 3 shows the decay curves for the weakly bound electrons from ZnS:Mn, Cu. The results indicate that the number of electrons showed exponential attenuation; the number of bound electrons is given by

$$n \propto e^{-t/\tau'} \quad (5)$$

where τ' (the lifetime of the weakly bound electrons) is, in figure 3(b), 1703 ns.

The Br^- , as the charge compensator for Cu^+ , enters the crystal lattice of ZnS and forms the donor energy level in crystal when ZnS materials were sintered under an $\text{NH}_4\text{Br} + \text{S}$

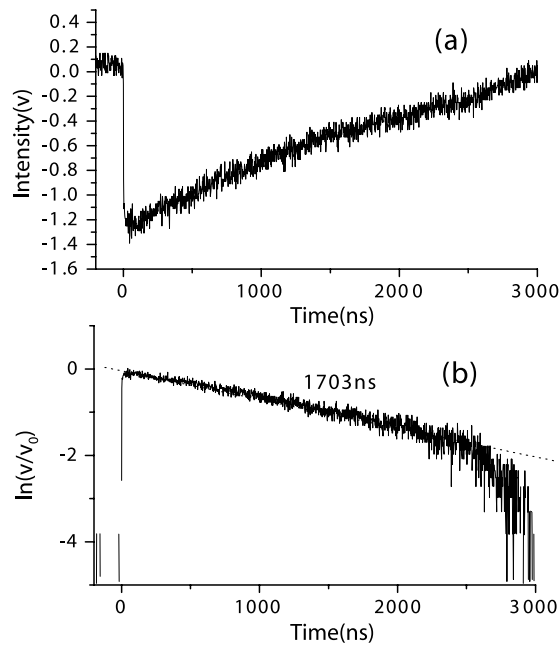


Figure 3. The decay curves for the shallow-trapped electrons of ZnS:Mn, Cu.

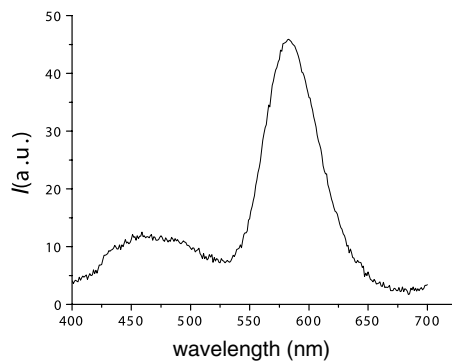


Figure 4. The photoluminescence spectrum for ZnS:Mn, Cu materials.

atmosphere [21]. The weakly bound electrons in shallow electron traps can return to the conduction band from the trap only when the electrons are disturbed with heat; therefore, the lifetime of these electrons is longer than that of the electrons in the conduction band.

4.2. The luminescent afterglow of ZnS:Mn, Cu materials

Figure 4 shows the photoluminescence spectrum for ZnS:Mn, Cu materials; the spectrum includes a blue belt (centre wavelength 450 nm), a green belt (centre wavelength 520 nm) and an orange belt (centre wavelength 585 nm). The blue and green belts are light from Cu^+ complex luminescent centres and the orange belt is that from Mn^{2+} separate luminescent centres.

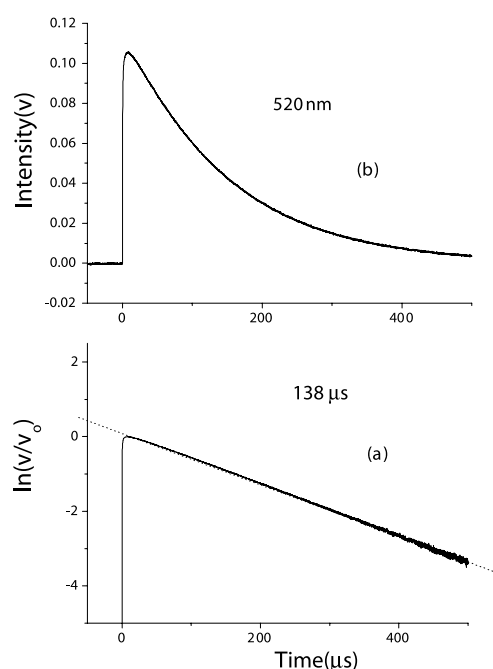


Figure 5. The luminescence decay curve for ZnS:Mn, Cu (excitation wavelength 355 nm).

Figures 5(a) and 6(a) show the decay curves for the fluorescence from Cu^+ green and blue luminescent centres. The exponential decay curves were observed (in figures 5(b) and 6(b)) with lifetimes of 138 and 140 μs , respectively.

In general, the doping with Cu^+ can cause complex luminescent centres to form and the lifetimes of the fluorescences from the blue and green centres are similar. The lifetime of the excited state of Cu^+ is much longer than that of the electrons in the conduction band. Therefore, there is a stronger luminescence from the Cu^+ luminescent centre, while the electrons in the conduction band disappear.

Figure 7(a) shows the decay curve of the fluorescence from the Mn^{2+} orange luminescent centre. An exponential decay was observed, with a lifetime of 680 μs (in figure 7(b)). Electrons transit from the valence band to the conduction band when ZnS:Mn, Cu materials are excited with a pulsed laser. Orange light, from the ${}^6\text{S} \rightarrow {}^4\text{G}$ transition in Mn^{2+} , was observed arising from separate Mn^{2+} luminescent centres under the excitation with electrons moving in the conduction band. The ${}^6\text{S} \rightarrow {}^4\text{G}$ transition in Mn^{2+} is forbidden in general; with the disturbance by the crystalline field, however, the electron transition will become permitted [19]. Where the process is only partially allowed and the transition probability is low, a relative long lifetime of 0.68 ms was obtained for the fluorescence afterglow from the Mn^{2+} luminescent centre. This longer fluorescence afterglow from the Mn^{2+} luminescent centre results in luminance saturation of ZnS:Mn, Cu luminescent materials excited with a high-frequency electric field.

The excitation spectra of ZnS, Mn, Cu were measured in [31, 32]. In the long-wavelength region of the excitation spectra, the spectrum of the green Cu^+ centre is very similar to that of Mn^{2+} , and their termination wavelengths are all 420 nm. This means that all electrons exciting the two emission centres are from the conduction band or a trap level.

The emission process of the Cu^+ centre is shown in figure 8. An electron in a conduction band or trap level falls to an excited state, E_1 , of an emission centre at first; it relaxes for a while

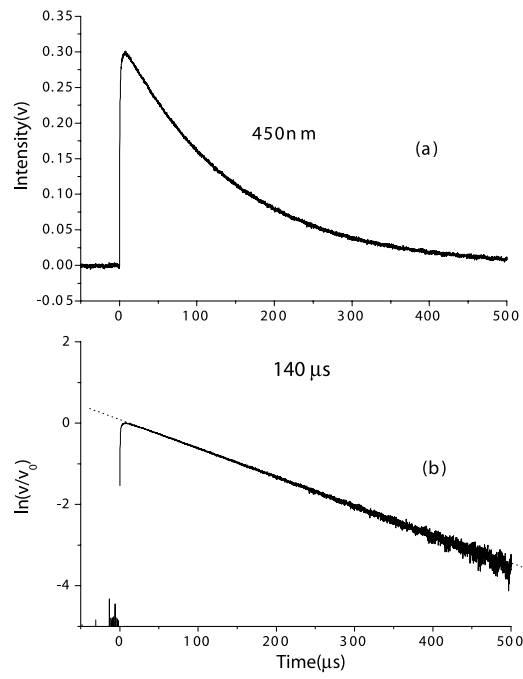


Figure 6. The luminescence decay curve for ZnS:Mn, Cu.

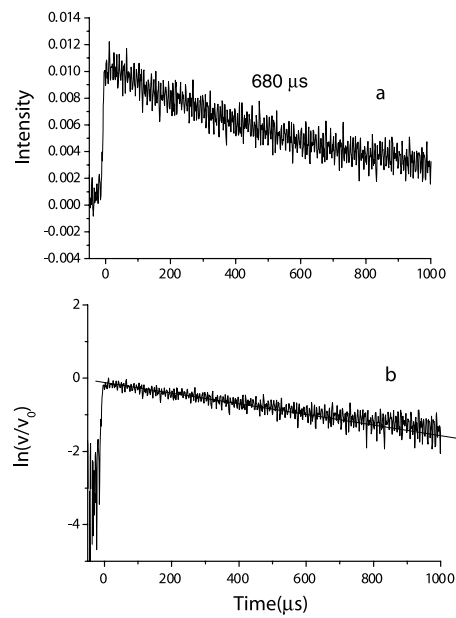


Figure 7. The luminescence decay curve for ZnS:Mn, Cu.

at E_1 and then jumps to the ground state E_2 with luminescence. The fluorescence afterglow is due to the relaxation time at E_1 .

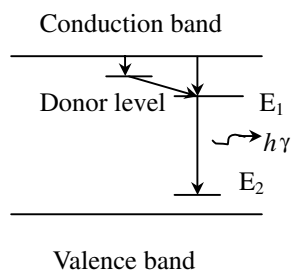


Figure 8. A schematic diagram of the Cu^+ centre luminescence.

5. Conclusions

Precision measurements of the changes undergone by photocarriers from ZnS:Mn, Cu luminescent material together with the investigation of the complex decay processes underlying the fluorescence for photocarriers can be carried out using the microwave absorption dielectric spectrum detection technique combined with short-duration-pulse laser measurement techniques. Exponential fluorescence decay processes were observed for three luminescent centres in ZnS:Mn, Cu luminescent materials; lifetimes of 1177 and 1703 ns were obtained for the electrons in the conduction band and the weakly bound electrons, respectively. The lifetimes of the excited state were found to be 138, 140 and 680 μs for blue Cu^+ , green Cu^+ and Mn^{2+} luminescent centres, respectively.

The entire processes of excitation and luminescence and the luminescent phenomenon can be understood in depth by means of systematic study of the decay processes and fluorescence decay processes for the photoelectrons.

Acknowledgment

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