Nature of luminescence transition in low-resistivity n-type ZnS single crystals

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The cathodoluminescence spectra of low-resistivity n-type ZnS single crystals were recorded. The emission peak energy shifted towards higher energies with a corresponding decrease in the half-width of the emission band as the temperature was decreased. Time-resolved emission spectra and the decay of luminescence were measured at 77 K, in which the energy of the emission band at its maximum shifted to lower energies during decay. The decay of luminescence was found to be non-exponential. These studies gave experimental evidence that the blue self-activated emission of low-resistivity n-type ZnS crystals is of the donor–acceptor pair transition nature, and thereby the difference of emission peak energy for emitting ZnS diodes with different Schottky contacts was interpreted.

1. Introduction

In previous work, on blue light emitting ZnS diodes [1], the electroluminescence spectra for emitting ZnS diodes revealed a broad emission band at 470 nm (2.63 eV) and 490 nm (2.53 eV) for emitting ZnS diodes with silver and gold as Schottky contacts, respectively. The shift in the electroluminescence emission peak was also observed by Lawther and Woods [2] for ZnS diodes prepared by depositing gold, platinum or silver as Schottky contacts.

The reason for the difference in emission peaks of silver and gold diodes was not known. In the present work cathodoluminescence spectra as well as time-resolved spectra were recorded for the same low-resistivity ZnS single crystals used in diode fabrication. This work was undertaken to elucidate the nature of the luminescence centre and the type of transition responsible for the emission from ZnS-type crystals, and thereby to find the reason for the shift in emission peak with change of Schottky contact.

2. Experimental techniques

Single crystals of zinc sulphide were grown from high-purity Optran ZnS powder using a Bridgman method under an argon gas pressure of 7×10^6 Pa at 1850° C. X-ray studies showed that the crystals grown exhibited hexagonal structure. Low-resistivity n-type ZnS single crystals were achieved by firing the as-grown high-resistivity ZnS single crystals in molten Zn–Al alloy. Two methods of heat treatment described in detail in the previous paper [1] were used. In the first method the as-grown ZnS dice were fired in a quartz ampoule containing molten Zn–0.5% Al–1% Ga at 1000° C for 200 h. The second sample was prepared by firing the as-grown dice in a graphite crucible containing molten alloy of Zn–10% Al at 1000° C for 100 h. The two fired samples were found to be n-type

ZnS with a low resistivity of about 10^3 and $10^2 \, \Omega \text{cm}$, respectively [1].

For cathodoluminescence emission spectra measurements, each sample was mounted on the cold finger of a liquid helium cryostat. The cryostat was evacuated to a pressure of 5×10^{-5} Pa and the sample was excited with a scanned 10 keV electron beam at current densities up to $200 \, \mu\text{A cm}^{-2}$. The emission of the sample was mechanically chopped at 800 Hz and analysed by a 1 m Hilger Monospek monochromator equipped with a grating of 1200 lines per millimetre blazed at 500 nm. Emission spectra were detected by an EMI 6255B photomultiplier tube and recorded using a low-noise amplifier, phase-sensitive detector and potentiometric recorder. Sample temperatures in the range 4.2 to 77 K were measured by means of a gold–iron against Chromel thermocouple and by a copper–constantan thermocouple for the temperature range 77 to 293 K. Decay curves and time-resolved emission spectra were measured by pulsing the electron beam at 10 kHz with a pulse width of 50 μsec. The pulsed emission was reflected through 45° and directed through the slits of the monochromator. A photomultiplier at the exit slit of the monochromator was used to detect the analysed pulsed emission. The output of the photomultiplier was fed into a boxcar detector, together with a reference signal from the generator. The boxcar output was displayed on an oscilloscope and fed into a pen recorder.

3. Experimental results

The cathodoluminescence emission spectra of the as-grown ZnS single crystals at 77 and 4.2 K are shown in Fig. 1. At 4.2 K the emission spectrum showed a free exciton at 326.6 nm, structured edge-emission centred at 343.75 nm, a blue broad emission band at 416 nm and a green emission band at 520 nm.
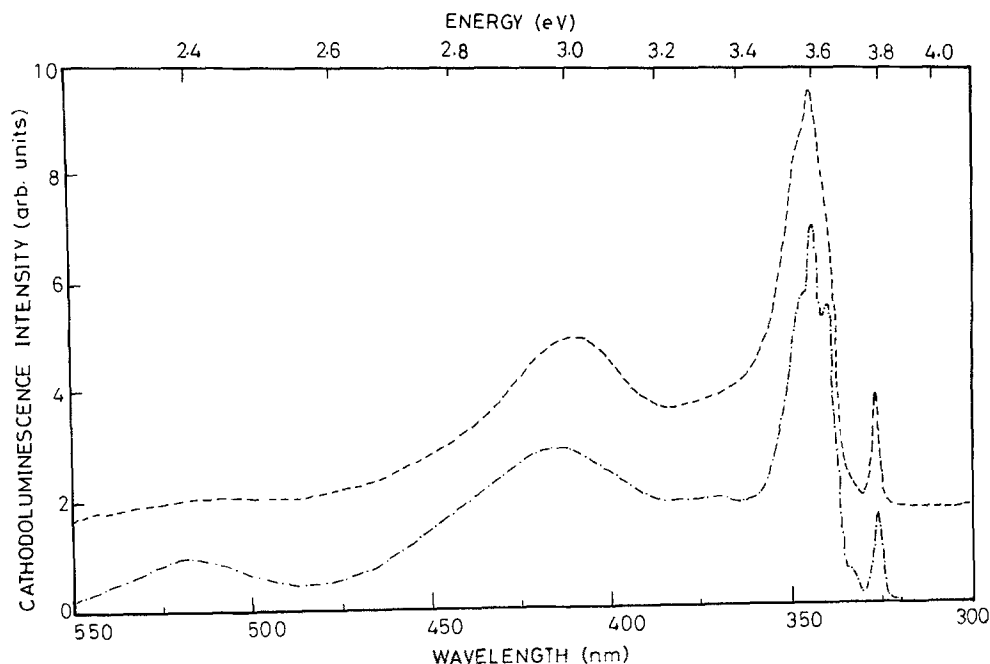
Figure 1 The cathodoluminescence emission spectra of as-grown ZnS single crystal at (– – –) 77 K and (–·–·–·–) 4.2 K.

On increasing the temperature of the sample to 77 K the edge emission became less structured, the blue broad emission band shifted slightly to about 410 nm and the intensity of the green emission band tended to decrease. The edge emissions have been observed by many authors [4–6] in pure ZnS single crystals as well as in low-concentration doped ZnS single crystals, and were attributed to donor–acceptor (DA) pair recombination. The blue and green emission bands resemble blue and green copper emissions and were attributed to the copper impurity already present in the Optran ZnS powder used for crystals growth [6].

Fig. 2 shows the emission spectra at 293, 77 and 4.2 K of low-resistivity (10^3 Ω cm) ZnS single crystals after firing the as-grown crystals in molten Zn–0.5% Al–1% Ga alloy at 1000° C for 200 h (Sample S-1). At 293 K the sample showed a high-intensity blue emission peaking at 460 nm (2.70 eV) which shifted to higher energy on decreasing the sample temperature to 77

and 4.2 K. Fig. 3 shows the emission spectra at three temperatures (4.2, 77 and 293 K) for low-resistivity (10^2 Ω cm) ZnS–Al single crystals (Sample S-2), produced by heat treatment of the as-grown ZnS single crystals in a graphite crucible containing molten Zn–10% Al alloy at 1000° C for 100 h. At 293 K, a broad emission band appeared at 465 nm (2.67 eV) and shifted to 443 nm (2.8 eV) and 439 nm (2.83 eV) at 77 and 4.2 K, respectively. The half-width of the emission band for both samples showed an increase with increase of temperature; it increased from about 0.36 eV at 4.2 K to 0.44 eV and 0.53 eV at 77 and 293 K, respectively.

The time-resolved emission spectra for both low-resistivity n-type ZnS single crystals (Samples S-1 and S-2) are shown in Figs 4 and 5, respectively. The emission spectra obtained at times of 0, 2, 5, 10 and 20 μsec after the excitation ceased showed a pronounced continuous shift to lower energies which
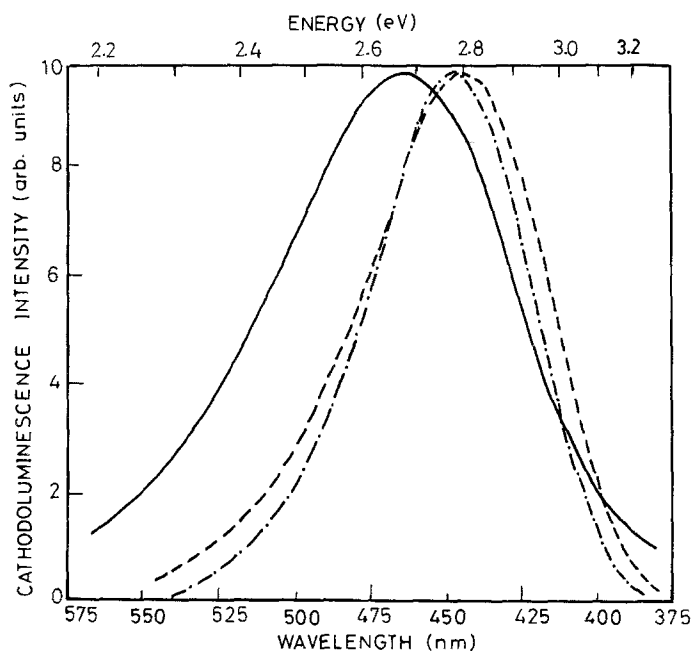

Figure 2 The cathodoluminescence emission spectra of low-resistivity n-type ZnS single crystal Sample S-1 (~10^3 Ω cm) at (———) 293 K, (– – –) 77 K and (–·–·–·–) 4.2 K.

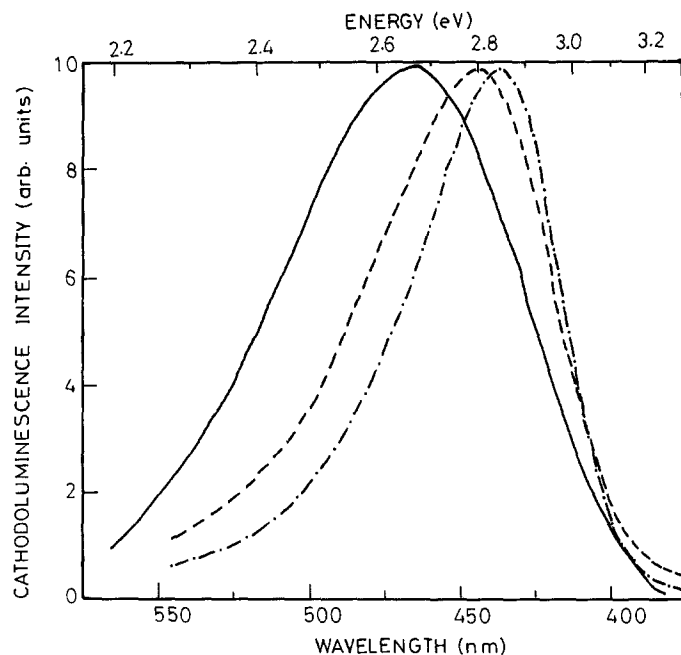*Figure 3* The cathodoluminescence emission spectra of low-resistivity n-type ZnS single crystal Sample S-2 ($\sim 10^2\,\Omega\,\mathrm{cm}$) at (———) 293 K, (– – –) 77 K and (–·–·–·–) 4.2 K.

confirmed the DA pair transition mechanism for the luminescence. The decay curves of the emission at the peak position for the two samples at 77 K are illustrated in Fig. 6. The decays were non-exponential and consisted of two components, characterized by initial decay times of 4.4 and 2 μsec until the intensity of the emission decreased to 1/e of the initial values for S-1 and S-2, respectively.

4. Discussion

Heavy doping of the high-resistivity ZnS single crystals with aluminium in the presence of molten zinc converted them to low-resistivity n-type crystals; this treatment increased the aluminium donors in the host lattice and reduced the compensation of donors by decreasing the number of zinc vacancies. Cathodoluminescence of these crystals gave a broad blue emission near 465 nm (2.66 eV) at 293 K, which shifted towards higher energies with a corresponding decrease in the half-width of the emission band as the tempera-

ture decreased. The half-width decreased from about 0.53 eV at 293 K to 0.44 eV at 77 K and 0.36 eV at 4.2 K. The position of the emission band maximum depended critically on the aluminium doping level as well as the degree of zinc extraction in the sample, and shifted towards high energy with increasing aluminium concentration (see cathodoluminescence of S-1 and S-2 at 77 K and 4.2 K in Figs 2 and 3, respectively). The blue emission peak shifted markedly to lower energy during the luminescence decay (see Figs 4 and 5), which is a feature of DA emission [7, 8].

The self-activated (SA) blue emission in aluminium- or chlorine-doped ZnS has been known for a long time as a characteristic emission of these phosphors. The luminescent properties of the SA band have been investigated by many workers and the DA pair nature of the SA centre has been elucidated [7–9]. The concept of DA pair emission was first proposed by Prener and Williams [10] and was established by Hopfield *et al.* [11]. The energy of emission due to the transition
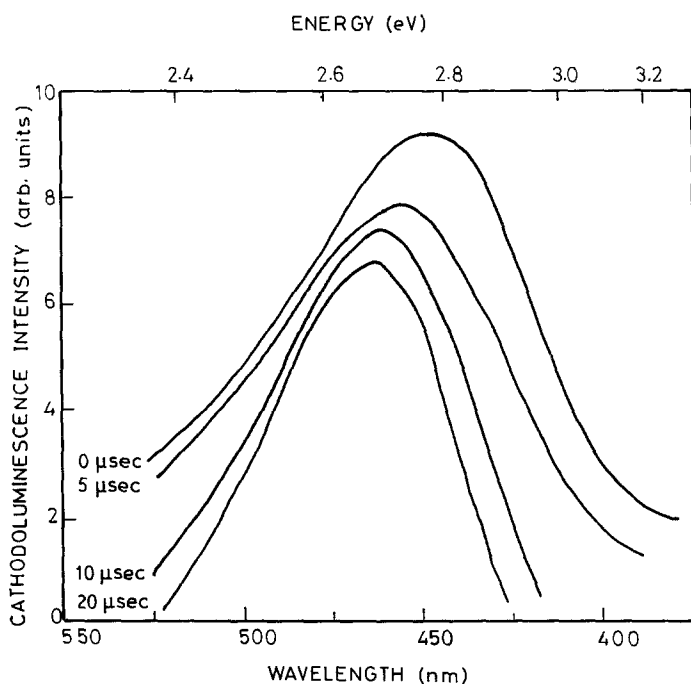

Figure 4 Time-resolved spectra of the emission band in ZnS Sample S-1 at 77 K. Intensities measured at times of 0, 5, 10 and 20 μsec after excitation by 200 μA cm^{-2} of 10 keV electrons.
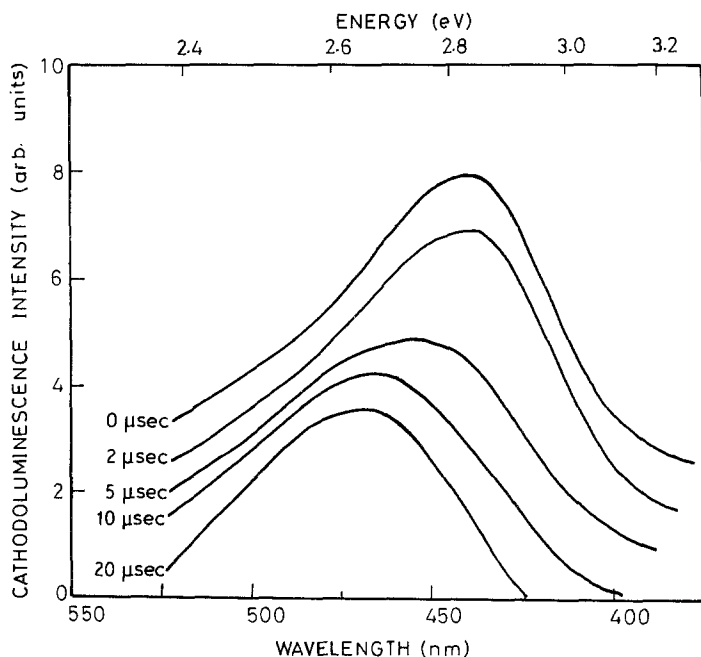
from donor-like level to acceptor-like level in a pair was given by the well-known expression [11]

$$E(r) = E_g - (E_A + E_D) + \frac{e^2}{\varepsilon r}$$

where E_g is the band gap energy, $E_D(E_A)$ is the donor (acceptor) binding energy and $e^2/\varepsilon r$ is the Coulombic interaction between donors and acceptors separated by a distance r; ε is the dielectric constant at low frequency. An increase of the concentration of donors or acceptors or both will cause a decrease in the mean DA pair separation which, by consideration of the above equation, shows that the emission energy increases [12]. The difference in emission energy at low temperatures for Samples S-1 and S-2 can be explained when it is considered to be due to an increase of the concentration ratio of the isolated aluminium donors to the zinc vacancies after heat treatment of the single crystals in molten Zn–Al alloy at different times and different aluminium concentrations.

The blue emission peaks for both samples shifted to lower energies during the decay, which is the feature of DA pair emission and is consistent with that reported by Era and co-workers [7, 8]. The probability of a transition between pairs separated by distance r is proportional to exp $(-2r/a_D)$ [13] where a_D is the radius of the donor state. As a result, in DA pair transitions the peak energy will vary with the intensity of the excitation used. As the excitation intensity is increased the emission due to distant pairs will saturate first, because of the lower probability of recombination for the more distant pairs. This will be followed by the transitions arising from the closer pairs involved in the emission, and the energy of the emission will increase.

If the excitation is removed and the energy of the emission observed during the decay, it is found that the energy of the emission decreases. This is because the closer pairs recombine more rapidly because of the larger transition probability, so that the relative number of distant pairs increases. Therefore as the decay progresses the relative number of transitions arising from the more distant pairs increases and the energy of the emission decreases. Consequently when an emission moves to higher energies as the intensity of excitation is increased and shifts to lower energies
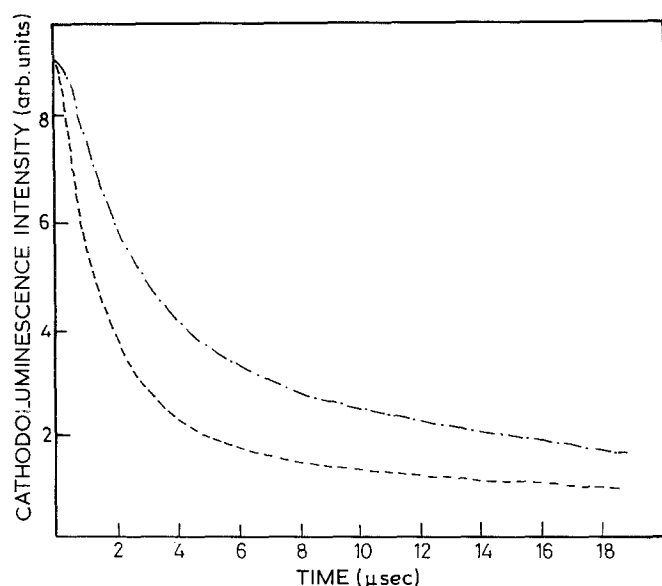
during decay, the emission is assumed to be due to DA pair transitions. The energy of the DA emission changes with temperature in the same direction as the band gap, i.e. as the temperature rises the energy decreases. DA pair transitions follow biomolecular decay characteristics. A given decay is often found to be non-exponential and usually has two components superposed upon one another. This type of decay is due to the presence of traps which introduce an independent mechanism into the decay characteristics.

In the present work, the cathodoluminescence emission properties of low-resistivity n-type ZnS single crystals which were characterized by a shift to higher energy with lowering temperature, a low energy shift during decay, and also a non-exponential decay of the emission at low temperature, give an indication of the DA pair transition mechanism responsible for this type of emission.

In view of these facts, the difference in peak energies of the electroluminescence for diodes with different Schottky contacts in the previous work [1] can be attributed to changes of the excitation intensity and decay time of the luminescence process.

In conclusion, the cathodoluminescence emission spectra at different temperatures, the time-resolved spectra, and the decay curves at the emission peak wavelength of n-type low-resistivity ZnS gave the clearest experimental evidence that the blue emission of zinc sulphide heavily doped with aluminium is of the self-activated emission type. This emission can be explained by the DA pair transition mechanism, i.e. as due to the recombination of the electron at an isolated aluminium donor with the hole at an Al–Zn vacancy complex acceptor.

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