JOURNAL OF MATERIALS SCIENCE 21 (1986) 3227–3230

Blue light emitting ZnS diodes

A. ABDEL-KADER,
Physics Department, Faculty of Science, Menoufia University, Menoufia, Egypt
F. J. BRYANT
Department of Physics, University of Hull, Hull, UK

Low resistivity n-type ZnS single crystals of about $10^3\,\Omega$ cm and $10^2\,\Omega$ cm were achieved by firing the as-grown high resistivity ZnS single crystals using quartz ampoules and graphite crucible, respectively. Schottky diodes fabricated from sample I gave stable blue emission in reverse bias while sample II gave blue emission in forward bias. The characteristics of these diodes were studied and presented. Carrier concentrations were estimated from the capacitance–voltage measurements of the two types of diodes. Electroluminescence spectra as well as cathodoluminescence spectra of both samples are presented. The blue emission peak was ascribed to the donor–acceptor pairs transition.

1. Introduction

ZnS is a semiconductor with a direct band gap of 3.65 eV at room temperature. Because of its wide band gap it is a promising material for blue emitting diodes. In general the most efficient structures for light emitting diodes are the p–n junctions. The as-grown ZnS single crystals have high resistivities of 10^{10} to $10^{12}\,\Omega$ cm, these crystals can be converted to low resistivity n-type material by doping the host crystals with group III elements such as aluminium, gallium and indium in the presence of zinc vapour at high temperature [1–3]. This treatment introduced the donors in the host crystals and reduced the compensation of donors by decreasing the number of zinc vacancies formed during the crystal growth and its doping. ZnS exhibit only n-type; to our knowledge all attempts for obtaining p-type ZnS have been unsuccessful [4]. The main problem is thus to find ways to inject minority carriers by other means than the p–n junction. In most cases low ohmic crystals were equipped with rectifying contacts and light emissions were obtained in some cases in forward bias [4–8], and in other cases in reverse bias [9–11]. The presence of a thin layer of high resistivity ZnS on the low resistivity ZnS crystals was essential for the high efficiency of the light emitting diodes [8].

In the present work stable bright blue emitting diodes were achieved to give emission in reverse bias as well as diodes to give emission in forward bias.

2. Experimental procedures

ZnS single crystals were grown by a Bridgman method under an argon gas pressure of about 7×10^6 Pa at 1850° C. These ZnS single crystals exhibited high resistivities of 10^{10} to $10^{12}\,\Omega$ cm. The low resistivity n-type ZnS single crystals (samples I) were conducted by firing some chips of the as-grown single crystals in a sealed quartz ampoule containing molten Zn + 0.5% Al + 1% Ga alloy at 1000° C for about 200 h and followed by rapid quenching in air. This treatment reduced the bulk resistivity of ZnS to about $3 \times 10^3\,\Omega$ cm. Other lower resistivity single crystals (samples II) were obtained by firing the as-grown ZnS single crystals in graphite crucible containing molten Zn + 10% Al alloy at 1000° C for 100 h and then followed by rapid quenching in air [12]. The resulting low resistivity ZnS single crystals were cleaved into dice, each of approximate dimensions of 4 mm × 2 mm × 1 mm. Ohmic contacts were made by wetting the freshly-cleaved surface with a mixture of 25% indium and 75% gallium, and more indium was added by the soldering gun, then subsequently heated at 385° C for 4 min in an argon atmosphere. The Schottky contacts were made by evaporating gold layer of 1 mm^2 area onto the opposite high resistivity surfaces of the dice at a pressure of 10^{-7} torr. The contact area was conducted in good accuracy by masking the whole sample except this area during evaporation, the contact area was also checked and measured under a microscope. The diode was mounted on a transistor header using silver paste. The current–voltage (I–V), brightness–voltage (B–V) and capacitance–voltage (C–V) characteristics of the devices were measured. Electroluminescence spectra of the blue emitting Au–ZnS–In and Ag–ZnS–In diodes were measured at room temperature. Also cathodoluminescence spectra of both low resistivity ZnS single crystals used for diodes fabrication were measured at 293, 77 and 4.2 K.

3. Results and discussion

3.1. Emitting diodes in reverse bias

The current–voltage as well as the brightness–voltage characteristics at 293 K of the typical Ag–ZnS–In and Au–ZnS–In diodes made from samples I were shown in Fig. 1. All the diodes fabricated showed stable bright blue emissions with threshold voltages between 9 to 11 V when silver or gold contacts were negative i.e. in the reverse direction. Some of these diodes showed as well a faint blue emission in the forward direction but it was quenched after a short

0022-2461/86 $03.00 + .12

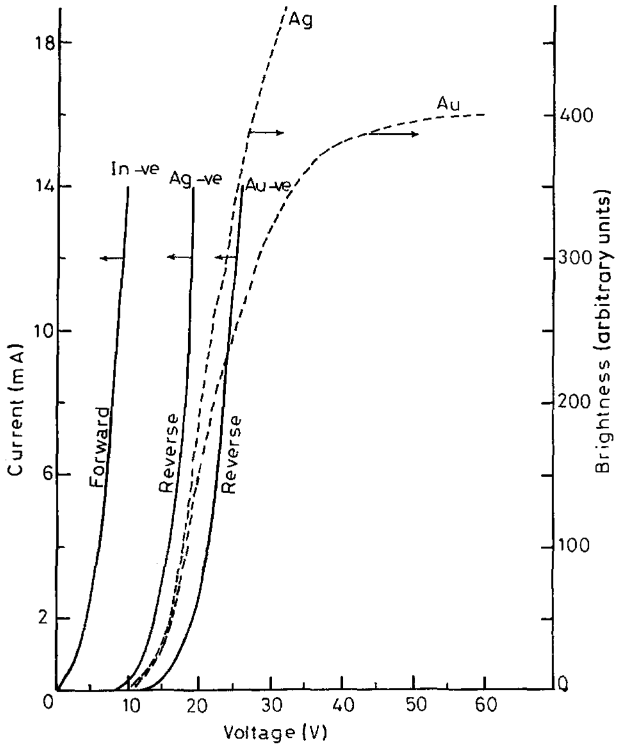

Figure 1 The current–voltage and brightness–voltage characteristics of Ag–ZnS–In and Au–ZnS–In blue emitting diodes fabricated from sample I at 293 K.

time of working. The devices with gold contacts were stable for a long time of working while that with silver contacts showed some deterioration.

The carrier concentration N_C is related to the capacitance–voltage of the device in reverse bias by the following equation [13]

$$N_C = \frac{2}{e\varepsilon_0\varepsilon_s A^2\left[d\left(\frac{1}{C^2}\right)\Big/ dV\right]} \qquad (1)$$

where C is the contact capacitance of the device, ε_s is the dielectric constant of ZnS [14]; ε_0 is a constant $= 8.85 \times 10^{-12}\,\mathrm{F\,m^{-1}}$; A is the contact area and e is the electron charge. Plots of C^{-2}–V for diodes with silver or gold Schottky contacts in reverse biases are shown in Fig. 2, from which the carrier concentrations of 10^{15} to $5 \times 10^{16}\,\mathrm{cm^{-3}}$ were estimated. These values of carrier concentrations have been calculated on the assumption that the dielectric constant is equal to the value of the high resistivity ZnS layer present under the Schottky contact [7]. The presence of high resistivity layer of ZnS under the gold

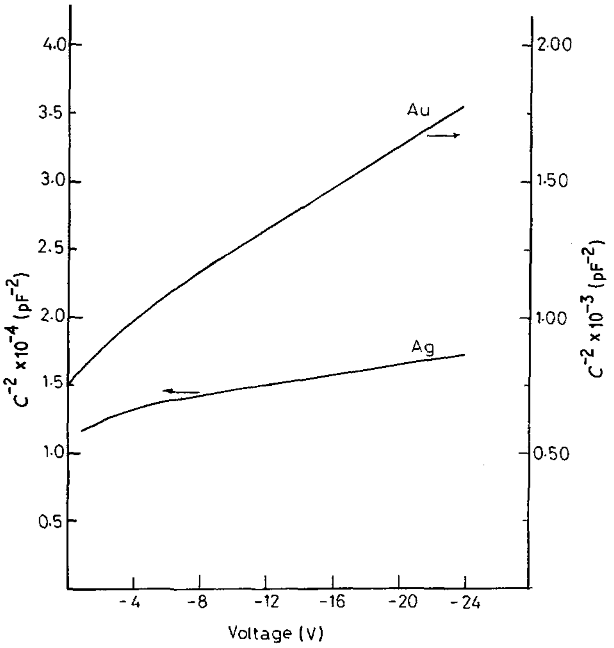

Figure 2 The capacitance–voltage characteristics of Ag–ZnS–In and Au–ZnS–In blue emitting diodes at 293 K (sample I).

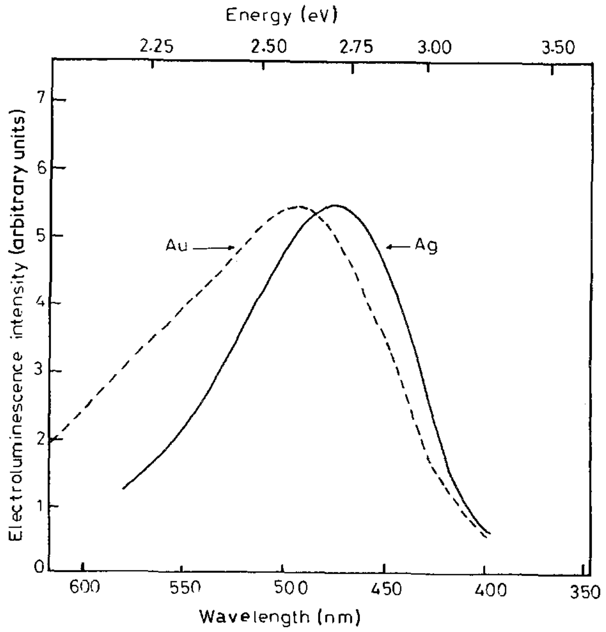

Figure 3 Electroluminescence emission spectra of Ag–ZnS–In and Au–ZnS–In diodes at 293 K (sample I).

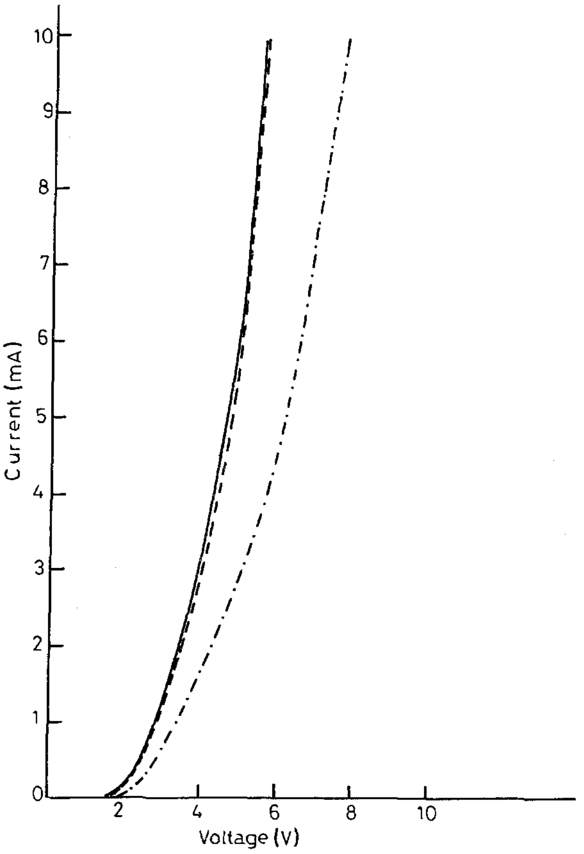

Figure 4 The current–voltage characteristics of the Au–ZnS–In diodes fabricated from sample II at 293 K in forward direction. (——) D1; (– – –) D2; (–·–) D3.

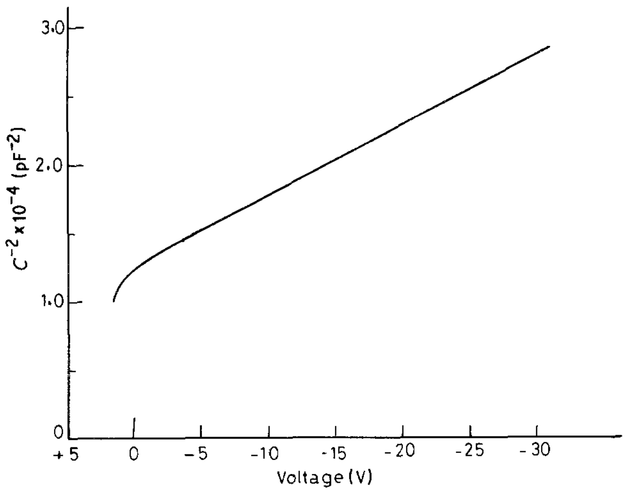

Figure 5 The capacitance–voltage characteristic of Au–ZnS–In diode under reverse bias at 293 K (sample II).

or silver contacts was indicated from the high values of the intercept on the voltage axis; the barrier heights of 1.65 and 2 V were reported for silver and gold, respectively [13]. The depletion region widths of the devices at the silver and gold contacts were 9.6×10^{-5} and 6.7×10^{-4} cm, respectively, at a voltage of about 10 V, the field strength in the depletion region was of the order 1.5×10^4 to 10^5 V cm^{-1}, this field strength is sufficient to accelerate the electrons from the metal in the depletion layer and make them "hot" enough to impact–excite the luminescent centres. The field strength in the depletion layer suggested impact excitation rather than minority carriers inject, as a possible excitation mechamism for light emission of reverse biased Schottky diodes has been discussed by other investigators [10, 11, 15].

Electroluminescence spectra, for Ag–ZnS–In and Au–ZnS–In emitting diodes, at room temperature are shown in Fig. 3. The emission peaks were located at 470 nm (2.63 eV) and 490 nm (2.53 eV), respectively. The reason for the difference in emission peaks for silver and gold diodes is not known at present; it could be due to the change of field strength in depletion region of the two diodes, which in turn causes changes in electron current densities and acceleration of these electrons. It is interesting to note that the electroluminescence peak reported by other investigators [3] from the Au–Zn–In devices was slightly dependent on the polarity of applied voltage. The shift in emission peaks was also observed by Lawther and Woods [7] for devices prepared by depositing gold, platinum or silver as Schottky contacts.

3.2. Emitting diodes in forward bias

The resistivity of ZnS single crystals, fired in graphite crucible (sample II) was measured by the well known van der Paw method [16]; a method for measuring resistivity of a flat sample with arbitrary shape. The resistivity estimated was of the order of $2.7 \times 10^2\,\Omega$ cm which decreased by an order of ten than that obtained for sample I. This result could be explained as follows: in the case of samples fired in a sealed quartz ampoule, the higher resistivity obtained may be due to impurity contamination caused by the reaction between aluminium and silica during the heat treatment at 1000° C.

The reproducibility of the devices was shown from the current–voltage characteristics of three Au–Zn–In diodes in the forward direction illustrated in Fig. 4. These diodes showed good rectification in the reverse bias; at 10 to 15 V the current was of about 1 to 2 μA.

The barrier height of gold as a Schottky contact on ZnS was ~2 V which is consistent with other investigators [8]. The threshold voltage for blue emission observed by the unaided eye for these diodes was found to be 2.2 V and a stable bright blue emission was obtained at working potential of 5 to 6 V in

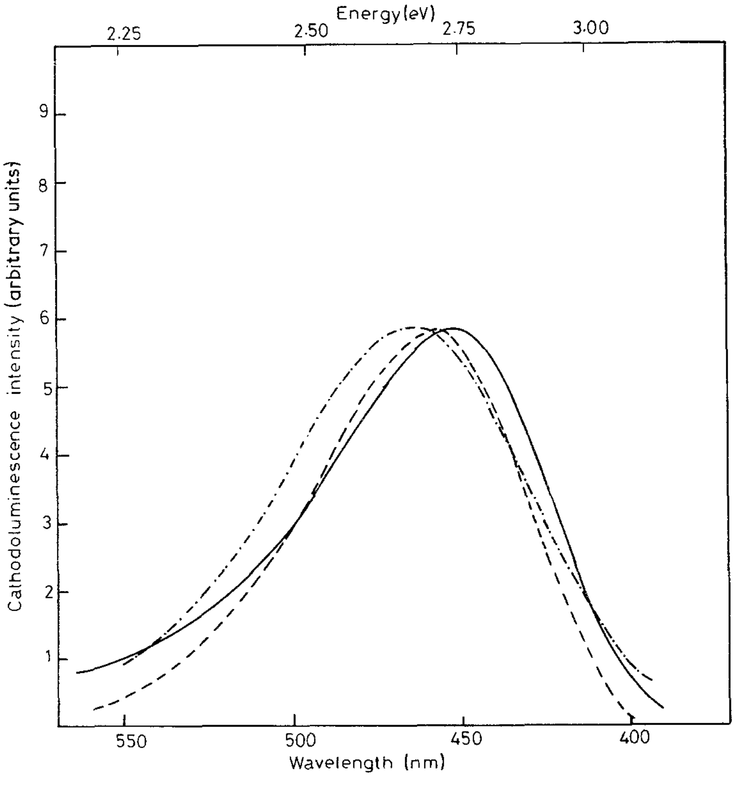

Figure 6 Cathodoluminescence emission spectra of the low resistivity ZnS single crystals fired at 1000° C in quartz ampoules containing molten Zn + 0.5% Al + 1% Ga alloy for 200 h (sample I). (–·–) 393 K; (– – –) 77 K; (——) 4.2 K.

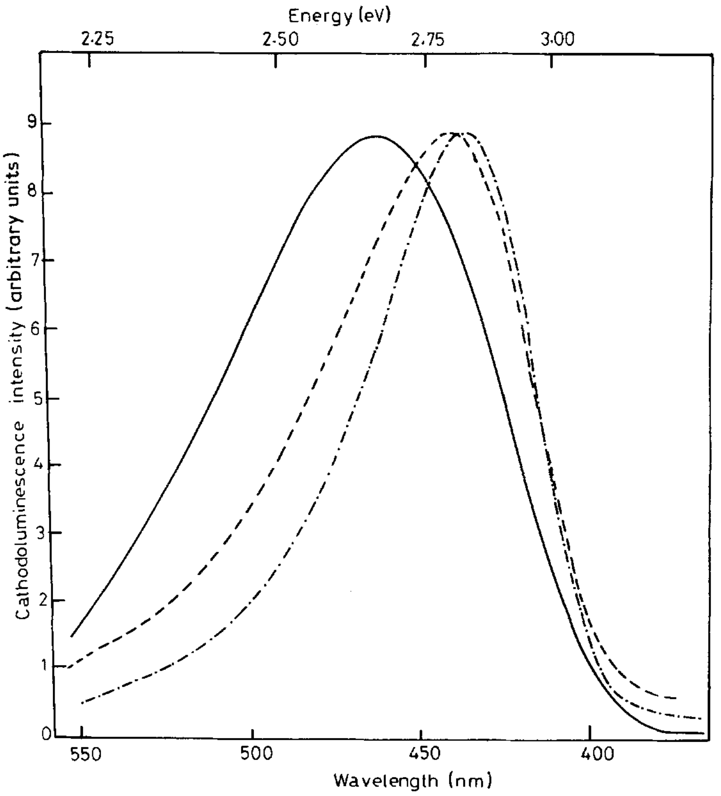

Figure 7 Cathodoluminescence spectra for ZnS single crystals fired in graphite crucible containing Zn–10% Al alloy at 1000° C for 100 h (sample II). (——) 293 K; (– – –) 77 K; (–·–) 4.2 K.

forward direction, whereas, no light emission was observed in reverse bias.

The capacitance–voltage characteristics of the Au–ZnS–In diode made was shown in Fig. 5, from the slope of the C^{-2}–V plot, the carrier concentration of $3.4 \times 10^{16}\,\mathrm{cm}^{-3}$ was estimated. The formation of insulating layer under the gold contact was indicated from the intercept on the voltage axis which is higher than the barrier height of gold on ZnS.

In order to find the nature of the emission, cathodoluminescence spectra of the low resistivity n-type ZnS single crystals (samples I and II) were studied at 293, 77 and 4.2 K in Figs 6 and 7, respectively. The broad band emission at 293 K centred at 2.67 eV shifted to higher energies of 2.80 and 2.82 eV at 77 and 4.2 K, respectively. It was also found, from the time-resolved spectra tested, that this emission peak shifed to lower energies during the decay of luminescence. These facts indicate that these blue emissions are of the donor–acceptor pairs type emissions. The electrons from the isolated aluminium donors recombine radiatively with the holes at the zinc vacancy–aluminium acceptor and give rise to the observed emissions.

In Section 3.1, the light emission under reverse bias was properly understood by the impact excitation mechanism, which suggested that electrons are injected from the metal Schottky contact into the depletion region and are accelerated by the field through it to impact–excite the luminescent centres. On the other hand the mechanisms responsible for the observed electroluminescence in forward direction seem to be rather complex. Up until recently, the model based on Auger recombination on the contact surface of the semiconductor was suggested and developed [4] to explain the light emission mechanism in forward direction.

In conclusion, blue light emitting diodes in a forward direction were obtained from the low resistivity ZnS crystals which have been achieved reproducibly by firing the as-grown crystals in Zn–10% Al alloy at 1000° C for 100 h using a graphite crucible as a container instead of a quartz ampoule. This material also showed a high cathodoluminescence emission at room temperature in the blue region, so it can be used as an efficient low-voltage cathodoluminescent ZnS phosphor.

References

1. M. AVEN and H. H. WOODBURY, *Appl. Phys. Lett.* **1** (1962) 53.
2. M. AVEN and J. Z. DEVINE, *J. Luminescence* **7** (1973) 195.
3. M. E. ÖZSAN and J. WOODS, *J. Phys. D., Appl. Phys.* **10** (1977) 1335.
4. N. B. LUKYANCHIKOVA, T. M. PAVELKO, G. S. PEKAR, N. N. TKACHENKO and M. K. SHEINKMAN, *Phys. Status Solidi* (*a*) **64** (1981) 697.
5. H. KATAYAMA, S. ODA and H. KUKIMOTO, *Appl. Phys. Lett.* **27** (1975) 697.
6. H. KUKIMOTO, S. ODA and H. KATAYAMA, *J. Luminscence* **12/13** (1976) 923.
7. C. LAWTHER and J. WOODS, *Phys. Status Solidi* (*a*) **50** (1978) 491.
8. *Idem, J. Luminescence* **18/19** (1979) 724.
9. C. C. YU and F. J. BRYANT, *Solid State Commun.* **28** (1978) 835.
10. N. T. GORDON, M. D. RYALL and J. W. ALLEN, *Appl. Phys. Lett.* **35** (1979) 691.
11. N. T. GORDON, *IEEE Trans. Electron. Devices* **ED-28** (1981) 434.
12. S. ODA and H. KUKIMOTS, *ibid.* **ED-24** (1977) 956.
13. M. SZE, in "Physics of Semiconductor Devices", 2nd Edn (Wiley, New York, 1981) p. 80.
14. S. S. DEVLIN, in "Physics and Chemistry of II-VI compounds", edited by M. Aven and J. S. Prener (North-Holland, Amsterdam, 1967) p. 603.
15. J. W. ALLEN, *J. Luminescence* **7** (1972) 228.
16. L. J. VAN DER PAU, *Philips Res. Rep.* **13** (1958) 1.

*Received 27 September
and accepted 30 October 1985*