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The fabrication of light-emitting devices from hot-pressed ZnSe powders

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A hot-pressing process was developed to synthesize fine ZnSe powders into compacts with high bulk density. The hot-pressed ZnSe powder compacts after an annealing treatment in the Zn–Al alloy melt were readily processed into light-emitting devices based on a metal–semiconductor (M–S) device structure. The fabricated devices are found to emit light in the orange region of the visible spectrum and have a room temperature quantum efficiency of the order of 10^{-6} photons/electron in the reverse direction. The photoluminescence and electroluminescence characteristics of the hot-pressed ZnSe powder compacts are also found to be very similar to those observed in single crystal material.

1. Introduction

The photoluminescence and electroluminescence properties of ZnSe have been extensively investigated in the past few years because this II–VI compound has considerable potential as a light-emitting diode material, due to its inherent luminescent efficiency and the relative low cost of the material. Various groups of workers [1–9] have reported the realization of ZnSe diodes emitting in the orange region of the visible spectrum. These orange colour light-emitting devices were fabricated almost exclusively from single crystal ZnSe wafers utilizing either a metal–semiconductor (M–S) or a metal–insulator–semiconductor (M–I–S) device structure, although several workers [10–13] have recently claimed that type conversion can be achieved in the II–VI compounds by the ion-implantation technique and that p–n junction devices can be fabricated.

Single crystal ZnSe is generally grown from the melt under a zinc vapour or inert gas overpressure, or by the high-pressure Bridgman method. Crystals grown by these techniques frequently consist of a matrix of single crystallites of varying sizes. Although inadequate in terms of quality and size these crystallites can be used for device fabrication, as was demonstrated in some recent studies [14–17]. Fine ZnSe powders are readily available but their potential as a starting source for device fabrication has not been fully explored. There also seems to be a lack of information available in the literature concerning a dependable process which can be employed to synthesize these fine ZnSe powders in a suitable form for device fabrication.

This paper describes a hot-pressing (pressure sintering) process which has been successfully employed to synthesize fine ZnSe powders into compacts with high bulk density and suitable for device fabrication. Devices based on a metal–semiconductor (M–S) structure are found to emit light in the orange region of the visible spectrum. The room temperature photoluminescence and electroluminescence characteristics of the hot-pressed ZnSe material and the ZnSe single crystals are compared in the present study.

2. Experimental procedure

The hot-pressing assembly used in the investigation is shown in Fig. 1. The graphite die–plunger unit was supported by a pair of steel rods and end-plates. They were enclosed by a quartz tube and were placed on the platform of a hydraulic press. The assembly was maintained in a flowing argon atmosphere and heated by a RF generator. The

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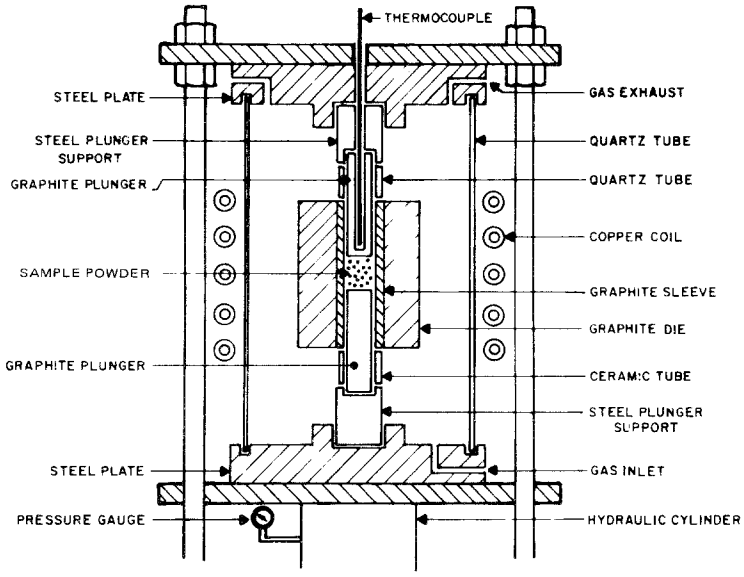

Figure 1 Schematic drawing of the hot-pressing assembly.

temperature was measured with a pair of Pt–Pt + 13%RH thermocouples and the pressure was applied manually. A temperature of 900° C and a pressure of 10 000 psi for a period of 60 min were found to be the best hot-pressing conditions which produced powder compacts of high quality and suitable for device fabrication.

The fine ZnSe powders used in the investigation were 99.999% pure and were obtained from the Harshaw Chemical Company in the USA. A large portion of the powders consist of grains in the 20 to 60 μm range and a small portion in the 2 to 5 μm range. Prior to the start of the hot-pressing process, it was found necessary to grind the starting ZnSe powders in an agate mortar and pestle for about five minutes. This was carried out to break up some of the aggregated crystals and also allow mixing the different size grains more uniformly. The ground powders were then directly loaded into the graphite die–plunger assembly. The graphite die and the enclosing quartz tube were then placed on the platform of the hydraulic press and rapidly heated up to the required hot-pressing temperature. After about 15 min of temperature equilibration, the necessary uniaxial pressure was rapidly applied to the die. At the completion of the hot-pressing period, the die assembly was allowed to cool down gradually to room temperature with full pressure maintained at the die assembly during the cooling period. The residual carbon adhering to the surface of the hot-pressed compacts was subsequently removed by a gentle polish using Al_2O_3 abrasive.

For device fabrication, thin sections (about 0.50 mm thick) were cut from the hot-pressed compact and were polished on both surfaces. The polished sections and about 5 g of Zn (95%) + Al (5%) alloy ingot were placed in a graphite container which in turn was sealed in an evacuated quartz ampoule. An annealing cycle of 950° C and 48 h was used. After the annealing treatment, about 0.05 mm thick of the thin sections was removed from the surface by a gentle polish. This was done in order to remove any residual Zn–Al layer adhering to the surface. Alloy of In–Ga was used for contacts. Subsequent to the deposition of a contact on one surface, the thin sections were cut into chips measuring approximately 1.25 mm × 1.25 mm × 0.40 mm and the chips were then mounted using conductive silver epoxy and bonded on conventional transistor headers. Two diode configurations were fabricated. All diodes have the In–Ga contact on one side. In one set of diodes, a gold wire was directly bonded to the top surface of the chip using a parallel-gap wire bonder, resulting with a (Au–ZnSe–InGa) configuration. In the other set of diodes, a thin layer of In–Ga alloy was painted over one half of the chip surface and the gold wire was bonded to the In–Ga layer, resulting with a (Au–InGa–ZnSe–InGa) configuration.

A scanning electron microscope was used to examine the microstructure of the hot-pressed ZnSe compacts. Photoluminescence emission was excited by a pulsed argon laser operating at 4880 Å. The emission spectra were recorded using a 0.3 m

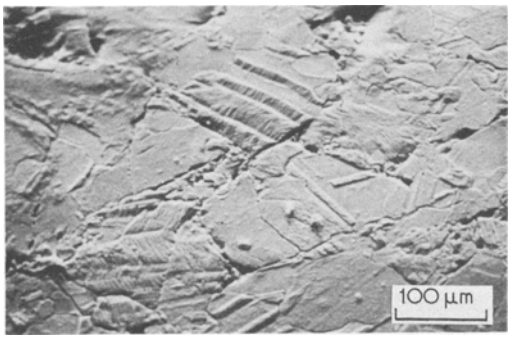

Figure 2 Scanning electron micrograph of the microstructure of a typical ZnSe powder compact hot-pressed at 900° C and 10 000 psi for 60 min.

scanning monochromator incorporating a (S-20) response photomultiplier. A Corning CS3-69 filter was used to shield the detector from scattered laser emission. The room temperature quantum efficiency of the fabricated devices was determined by the conventional integrating sphere technique.

3. Results and discussion

The hot-pressed ZnSe powder compacts were rigid and hard ceramic bodies and had a bulk density close to 95% of the theoretical value. Polished thin sections of the hot-pressed compacts were semi-transparent and non-brittle and exhibited no tendency to cleave in contrast to single crystal platelets of similar thickness. Fig. 2 is a scanning electron micrograph of the microstructure of a typical ZnSe compact hot-pressed at 900° C and 10 000 psi for 60 min.

At room temperature and under pulsed argon laser excitation, the hot-pressed ZnSe powder compacts exhibited broad band emission with a peak centred around 6400 Å and a half bandwidth of about 850 Å, as shown in spectrum A, Fig. 3. For comparison, an undoped ZnSe single crystal obtained from the Eagle Picher Company in the USA was excited under similar conditions. A broad band emission was also observed in this single crystal as shown in spectrum C, Fig. 3. It is apparent that the hot-pressed ZnSe powder compacts and the undoped ZnSe single crystal wafer exhibited essentially identical photoluminescence characteristics. The presence of grain boundaries and physical defects in the compacted solid did not appear to cause any modifications in the luminescent properties of the ZnSe materials. The emission peak at the 6400 Å region for undoped ZnSe has been attributed to a donor–acceptor pair recombination of the Cu impurity centres which are present in the ZnSe lattice as intrinsic impurities [18].

After similar annealing treatment in the Zn–Al alloy melt, both the hot-pressed ZnSe powder compacts and the Eagle Picher ZnSe single crystal also exhibited a broad band emission under laser photo-excitation, but they peak at slightly different region in the visible spectrum. The hot-pressed powder compact peaks at 6150 Å; whereas the single crystal peaks at around 6000 Å, as shown respectively in spectra B and D, Fig. 3. The annealing treatment of both the hot-pressed powder compact and the single crystal ZnSe has improved their photoluminescent emission efficiency. The emission peak at the vicinity of 6100 Å for ZnSe after annealing treatment in Zn–Al alloy has been interpreted by other workers [19] as a self-activation luminescence arising from a complex centre involving a Zn vacancy and an Al donor.

Under electrical excitation, the hot-pressed ZnSe devices exhibited broad band emission with a peak centred around 6000 Å and a half band-

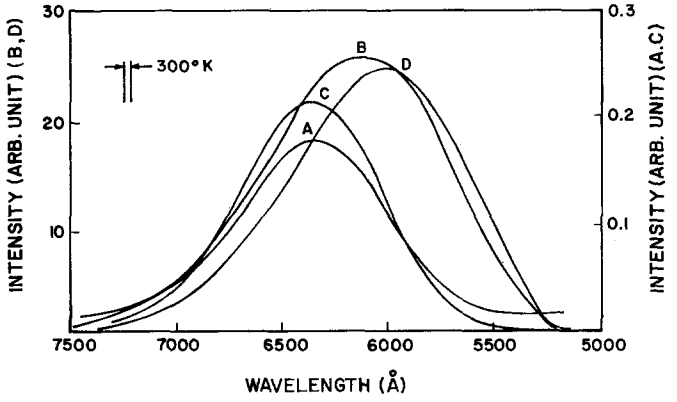

Figure 3 Room temperatue photoluminescence emission spectra of unannealed and annealed hot-pressed ZnSe powder compacts and single crystal ZnSe wafer: hot-pressed compact without anneal, A; hot-pressed compact with anneal in Zn–Al alloymelt, B; single crystal wafer (Eagle Picher) without anneal, C; single crystal wafer with anneal in Zn–Al alloy melt, D.

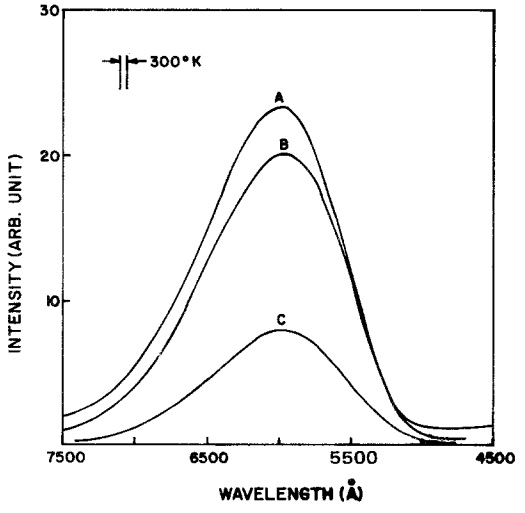

Figure 4 Room-temperature electroluminescence emission spectra of typical devices fabricated from hot-pressed ZnSe powder compacts and single crystal ZnSe wafer (Eagle Picher): (Au–InGa–ZnSe–InGa) device from single crystal, A; (Au–InGa–ZnSe–InGa) device from hot-pressed compact, B; (Au–ZnSe–InGa) device from hot-pressed compact, C.

width of about 1000 Å. The (Au–InGa–ZnSe–InGa) device configuration exhibited an electroluminescence in both forward and reverse directions, while the (Au–ZnSe–InGa) device configuration exhibited emission only in the reverse direction. In the present study, when the gold wire was biased positively and bulk semiconductor negatively, it is referred to as the forward direction and vice versa. In the reverse direction, the (Au–InGa–ZnSe–InGa) device configuration appeared to be significantly more efficient than the (Au–AnSe–InGa) device configuration, as shown in Fig. 4. Spectrum B, Fig. 4, shows the electroluminescence emission from the former device configuration and spectrum C shows the emission from the latter device configuration. For performance comparison, a (Au–InGa–ZnSe–InGa) device configuration fabricated from the single crystal ZnSe wafer exhibited almost identical electroluminescence characteristics as shown in spectrum A, Fig. 4. The dependence of electroluminescence emission intensity on device current between the hot-pressed and the single cyrstal ZnSe materials is shown in Fig. 5. Curve A was obtained from a device of single crystal; curve B was obtained from a device of powder compact hot-pressed for 60 min and curve C was obtained from a device of powder compact hot-pressed for only 15 min. It appeared that the device emission efficiency is improved by the extension of the hot-pressing period. This is probably due to a grain growth effect in the compacted solid. It is evident that the hot-pressed ZnSe powder compacts and the single crystal ZnSe wafer possess similar material properties and exhibit similar luminescent

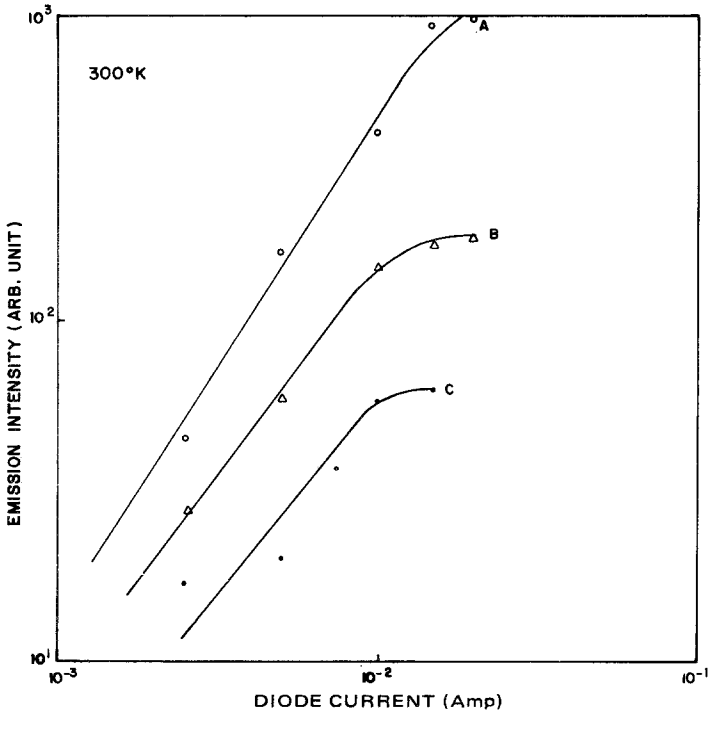

Figure 5 Dependence of electroluminescence emission intensity on device current for devices fabricated from hot-pressed ZnSe powder compacts and from single crystal ZnSe wafer using the (Au–InGa–ZnSe–InGa) configuration. Single crystal (Eagle Picher), A; powder compact hot-pressed at 900° C and 10 000 psi for 60 min, B; powder compact hot-pressed at 900° C and 10 000 psi for 15 min, C.

characteristics under electrical excitation. The mechanism of electroluminescence emission in the hot-pressed ZnSe powder compacts is likely due to an impact-ionization process. This observation is based on the assumption that the extensive annealing treatment of the hot-pressed powder compacts in the Zn–Al alloy melt has induced some partial substitution of the Zn ions in the ZnSe lattice with Al ions thus contributing a luminescent centre. Secondly, the (Au–InGa–ZnSe–InGa) and (Au–ZnSe–InGa) device configurations are essentially of the Schottky type. These two sources are therefore likely to promote an impact-ionization process for light emission as it has been observed in single crystal ZnSe material by other workers [1, 4, 7].

The room temperature quantum efficiency of the hot-pressed ZnSe devices was of the order of 10^{-6} photons/electron in the reverse direction and of 10^{-7} photons/electron in the forward direction. The (Au–InGa–ZnSe–InGa) device configuration was about 30% more efficient than the (Au–ZnSe–InGa) device configuration and the device efficiency of the single crystal material was about a factor of two higher than that of the hot-pressed powder compacts. The above efficiency values are slightly lower than some values reported by other workers and based on the single crystal materials [2, 5, 8, 9].

4. Conclusion

The present experimental investigation has demonstrated that light-emitting devices can be fabricated from very fine ZnSe powders and that the hot-pressing technique is an effective and reliable method in synthesizing the fine ZnSe powders into compacts with high bulk density which can be readily processed into light-emitting devices employing the metal–semiconductor (M–S) device structure. The hot-pressed ZnSe devices are found to emit light in the orange region of the visible spectrum. The photoluminescence and electroluminescence characteristics of the hot-pressed material are very similar to those observed in the single crystals. The room-temperature quantum efficiency of the hot-pressed ZnSe devices is, however, low and of the order of 10^{-6} photons/electron in the reverse direction and of 10^{-7} photons/electron in the forward direction. It is envisioned that an improvement in the device efficiency could be attained when larger grains of the starting ZnSe powders and a more extensive annealing treatment of the hot-pressed compacts are employed, as this may reduce the massive grain boundaries in the microstructure and also improve the grain-boundary conductivity. The present results seem to suggest that II–VI compound semiconductors in the polycrystalline form have similar potential as single crystal materials.

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