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PRODUCTION OF HIGH-CONDUCTIVITY N-TYPE ZnS, ZnSe, ZnS/ZnSe, OR ZnSe/ZnTe

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ABSTRACT OF THE DISCLOSURE

Zinc sulfide of either cubic or hexagonal crystalline form is made n-type by doping with halogen atoms while immersed in molten zinc. The preferred method of doping involves submerging the base crystal in molten zinc in the presence of iodine or of a heavy metal halide such as lead chloride or lead bromide. Best results are obtained when the starting material is also pre-doped with iodine or other halogen atoms, and when zinc sulfide powder is added to inhibit or prevent surface layers of the mother crystal from dissolving in the melt. Room temperature resistivities of the order of 1 to 10 ohm-centimeters or less are readily and reproducibly obtained. Zinc selenide and alloys or solid solutions of zinc selenide with zinc sulfide or with small proportions of zinc telluride may also be made n-type with the process.

A great deal of work has been done in the field of semi-conductor recombination light sources, and much current effort is directed to the development of such devices for emitting light efficiently in the visible light range. Most work of this sort has been concentrated on devices comprising III–V semiconductive materials such as gallium phosphide, gallium arsenide or gallium arsenide-phosphide. While II–VI compound semiconductors are generally characterized by wider band gaps and would therefore seem better suited for the development of visible light, they are not readily made in both n and p conductivity types and it has therefore not been feasible to produce p-n junctions with such materials. Indeed, zinc sulfide, which has the widest band gap of all of the compound semiconductors and is therefore potentially most attractive for use in visible light emitters, has not heretofore been readily susceptible to either p-type or n-type doping with high room temperature conductivity. In very recent years, there have been some reports in the literature claiming achievement of room temperature resistivities in the range from 1 to 10 ohm-centimeters for n-type zinc sulfide, but attempts to duplicate these results with the described processes have not been generally successful. Typical of such suggestions in the literature are processes involving aluminum doping by submerging zinc sulfide single crystal slices, cut along the {001} axis and polished, into zinc-aluminum alloys (from one to three percent aluminum) at 1050° centigrade for periods of from eight to fifteen days. Another procedure suggested in the literature involves the firing of cubic crystals of iodine-predoped zinc sulfide at 950° C. in liquid zinc. However, experience has shown that both of these processes require critical control of all operating parameters in order to obtain n-type conductivity at all, and also that the processes generally yield much higher resistivities than the desired 1 to 10 ohm-centimeters.

It is a principal object of the present invention to provide a new and improved process for making high conductivity n-type zinc sulfide (ZnS), zinc selenide (ZnSe), or solid solutions or alloys of zinc selenide with zinc sulfide or with a minor proportion of zinc telluride.

It is a further object of the invention to provide such a new and improved process which is capable of yielding end product materials with room temperature resistivities of the order of 1 to 10 ohm-centimeters or less.

Yet another object of the invention is to provide such a new and improved process which involves only simple and non-critical procedures and which reliably and reproducibly yields high-conductivity n-type ZnS, ZnSe, ZnS/ZnSe or ZnSe/ZnTe.

In accordance with the invention, the method of producing a material selected from the group consisting of ZnS, ZnSe, ZnS/ZnSe and ZnSe/ZnTe to impart n-type conductivity to such material comprises doping the material with halogen atoms while immersed in molten zinc. Preferably, the starting material is also predoped with iodine or other halogen atoms. The doping with halogen atoms while immersed in molten zinc is preferably accomplished by including a heavy metal halide, such as lead chloride or lead bromide, in the melt.

More particularly, in a preferred embodiment of the invention, a zinc sulfide crystal (either cubic or hexagonal) is dropped into a quartz capsule containing approximately 236 mg. of lead chloride and 0.1 to 0.2 gram of zinc. A quartz plunger is inserted into the capsule to keep the samples in the melt, with clearance provided between the plunger and the side walls of the capsule to permit the zinc melt to pass from one extreme of the capsule to the other. After insertion of the plunger, sufficient additional zinc to bring the total amount of zinc to 3.5 grams is added. Preferably, about 14 mg. of ZnS powder are also added to inhibit or prevent surface layers of the mother crystal from dissolving in the melt. The capsule is then evacuated to a pressure of 2×10^{-5} mm. of mercury or less, sealed off, and heated to approximately 950° C. for a four-day period. After heating, the capsule is removed from the furnace quickly, inverted and quenched in cold water. If desired, lead bromide or other heavy metal halide may be substituted for the lead chloride. Best results are obtained if the starting crystals of zinc sulfide are predoped with iodine, as by the use of iodine transport processes in the growth of the mother crystals; indeed, the use of halogen-predoped mother crystals yields end product resistivities which are consistently lower, by an order of magnitude of more, than those obtained by identical processing of previously undoped mother crystals.

An alternative process employs elemental iodine instead of the heavy metal halide. If combined zinc/iodine doping is to be employed, it is necessary to keep the iodine cool as by the use of liquid nitrogen, during evacuation of the capsule. This is achieved by using a quartz capsule with a side arm containing the iodine. After evacuation and immediately prior to sealing off of the capsule, the side arm containing the iodine is heated while the capsule is cooled to liquid nitrogen temperatures in order to transfer the iodine as a vapor to the doping interaction area. Best results have been obtained with starting crystals of cubic lattice configuration, by employing approximately 100 mg. of iodine and 3½ grams of zinc and by processing at 950° C. for 4 days, and again the use of iodine-predoped mother crystals and/or the inclusion of ZnS powder in the melt yields higher conductivity than that achieved with undoped mother crystals.

The dopant concentrations and the time and temperature conditions are not critical and may be varied within rather wide limits; in general, the use of higher dopant concentrations yields higher conductivity, and longer processing times yield thickner n-type films and consequently higher conductances. The processing temperature is preferably at or near the boiling point of zinc. The amount of molten zinc is not critical, so long as there is a sufficient amount to maintain immersion of the mother

crystal; the function of the zinc is to retard or prevent the formation of zinc vacancies in the mother crystal, either by in-diffusion of zinc atoms from the melt or by prevention of out-diffusion of zinc atoms from the lattice, or both. The suspension in the melt of a powder of the same composition as the mother crystal tends to presaturate the melt and thus reduces undesirable dissolution of surface portions of the mother crystal; again the amount or proportion of the added powder may be varied within wide limits, or may be omitted altogether, depending on the conductivity desired.

Either type of process may also be employed to produce high conductivity n-type ZnSe or ZnS/ZnSe; ZnSe/ZnTe with a minor proportion (less than 15%) of zinc telluride may also be made highly conductive n-type in the same manner.

The process yields n-type conductive films on the surface of the mother crystal, the film thickness being dependent primarily on the processing time and being in the vicinity of at least 5 to 20 microns with iodine-doped materials and much thicker when chlorine-doping is employed. Within the surface film produced by the processes of the present invention, resistivities of the order of 1 to 10 ohm-centimeters may be achieved with ZnS/ZnSe mixed crystals.

While particular embodiments of the invention have been described, it will be obvious to those skilled in the art that changes and modifications may be made without departing from the invention in its broader aspects, and, therefore, the aim in the appended claims is to cover all such changes and modifications as fall within the true spirit and scope of the invention.

I claim:

1. The method of producing a high conductivity n-type semiconductive material which comprises the steps of providing a crystalline starting material consisting essentially of a member of the group composed of ZnS, ZnSe, ZnS/ZnSe and ZnSe/ZnTe, which starting material has been predoped with halogen atoms, and treating said predoped starting material with halogen atoms while immersed in a zinc melt in an evacuated system.

2. The method of claim 1, in which said starting material is predoped with iodine atoms.

3. The method of producing high conductivity n-type zinc sulfide which comprises treating a crystalline starting material composed of halogen-predoped zinc sulfide in a zinc melt containing a halogen dopant in an evacuated system.

4. The method of claim 3, in which the halogen predopant is iodine.

5. The method of any preceding claim, in which said crystalline starting material is treated in a zinc melt containing a lead halide.

6. The method of any of claim 1–4 inclusive, in which said crystalline starting material is treated in a zinc melt in the presence of a halogen vapor.

7. The method of any of claims 1–4 inclusive, in which a powder of substantially the same composition as said starting material is suspended in said melt.

8. A method of producing a high conductivity wide band gap n-type semiconductive material which comprises the steps of providing a crystalline starting material consisting essentially of a member of the group composed of ZnS, ZnSe, ZnS/ZnSe and ZnSe/ZnTe, and doping said starting material with halogen atoms while immersed in a zinc melt containing in suspension a powder of substantially the same composition as said starting material.

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