Semiconductors, Vol. 39, No. 3, 2005, pp. 296–299. Translated from Fizika i Tekhnika Poluprovodnikov, Vol. 39, No. 3, 2005, pp. 316–319.
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ELECTRONIC AND OPTICAL PROPERTIES OF SEMICONDUCTORS

The Effect of Pressing on the Luminescent Properties of ZnS:Ga Powders

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Submitted June 23, 2004; accepted for publication August 9, 2004

Abstract—Zinc sulfide powders that have been doped thermally with gallium are studied. The mechanisms of Ga diffusion in the ZnS powders are considered in relation to the packing density of the powders' particles. To this end, some of the ZnS powders under study have been pressed into pellets. It is established that the doping of ZnS powders with Ga proceeds more efficiently if the powders have been compressed. The electroluminescence of ZnS doped with Ga is observed. © *2005 Pleiades Publishing, Inc.*

1. INTRODUCTION

The high emissivity and wide band gap of zinc sulfide (ZnS) make this material promising for the fabrication of optical devices that emit in a wide range of wavelengths [1]. The introduction of various impurities into ZnS makes it possible to obtain luminophors with specified properties [2]. However, in spite of numerous studies, the issues concerning effective methods of introducing these impurities into the ZnS matrix remain open [3]. The development of new technological methods of doping ZnS can, to a great extent, be conducive to a realization of the promising properties of this material. The introduction of impurities that act as coactivators (for example, gallium [4]) into ZnS is of special interest. This circumstance is all the more important since, at present, it is still not clear what the origin of the emitting centers significantly affected by Ga is or which structure involves Ga.

The purpose of this study was to gain insight into the diffusion mechanisms that are active during the doping of ZnS powders with Ga and to study the effect of Ga on the luminescent properties of ZnS in relation to the method used to introduce Ga into ZnS. The final objective of this study was a minimization of the concentration of extraneous impurities in powderlike ZnS after the thermal introduction of Ga.

2. EXPERIMENTAL

We studied powderlike ZnS (ETO.035.295 TY) in which the sizes of the particles were on the order of 15 μm (80% of the composition), and the sizes of the largest particles of the powder did not exceed 20 μm. The ZnS powder was pressed into pellets and annealed in the presence of metallic Ga for 1 h at a temperature of 800°C with a limited access to air. This limited access to air was attained using a gas seal made of activated carbon. After the annealing, the pellets were crushed. The obtained powder was then separated into two portions: the first portion contained the powder in which the sizes of the particles were no larger than 40 μm, and the second portion contained the powder in which the sizes of the particles exceeded 40 μm.

The photoluminescence (PL) and electroluminescence (EL) spectra were measured using a KSVU-23 system. The PL was excited by radiation from an LGI-23 nitrogen laser ($\lambda = 337.1$ nm). We used an alternating-voltage generator that operated at $U = 250$ V and $f = 5$ kHz. All the measurements were performed at room temperature.

The samples used for studying the EL were, in fact, electroluminescent indicators. They were fabricated using the conventional technology for powder luminophors: the structure included a transparent In_2O_3:Sn electrode deposited onto glass, a second electrode formed of metallic Al, and a light-emitting layer that was formed between the electrodes and consisted of a mixture of a powderlike ZnS:Ga luminophor and an insulating binder (an epoxy varnish). The thickness of the light-emitting layer was ~50 μm.

3. RESULTS

Studies of the fractional composition of the powder with respect to the sizes of the particles showed that the annealing of ZnS powder pressed into pellets at 800°C led to an increase in the sizes d of separate particles to values that exceeded 40 μm, irrespective of the presence of the Ga doping impurity. The volume fraction of the powder with $d \geq 40$ μm amounted to ~40% after annealing.

Since the PL studies showed that pressing did not affect the luminescent properties of the as-prepared (unannealed) ZnS powder, Fig. 1 shows the PL spectrum of only the pressed ZnS powder (curve *1*). As can be seen from Fig. 1, the PL spectrum of this powder is represented by a complex broad band with an emission peak at 500 nm and a half-width of 84 nm. The separation of the ZnS powder pressed and annealed at 800°C into two fractions (in which the size of the particles was larger and smaller than 40 μm) also showed that there were no differences (exceeding the measurement error) between the PL spectra of these two fractions. The annealing of the ZnS powder at 800°C (Fig. 1, curve *2*) led to a decrease in the band half-width to 67 nm and to a shift of the PL peak to a longer wavelength (λ_{max} = 515 nm) than the PL spectrum of the initial (unannealed) ZnS powder.

Interpretation of the luminescence band with its peak in the vicinity of 515 nm is ambiguous. For example, in [2, 5], this band was related to the O and Cu impurities in ZnS, while it was related to the emission of self-activated ZnS and also to the formation of anionic vacancies in [6, 7]. It is worth noting that the annealing-induced change in the spectral shape of the PL band occurs owing to a redistribution of the PL lines that form the band under consideration (Fig. 1). Bacherikov *et al.* [4] related this change in the spectral characteristics of ZnS powders to an increase in the concentration of sulfur vacancies (V_S) at the surface and also to the surface being relieved of radicals; as a result, the intensity of the band with λ_{max} = 520 μm increases and the nonradiative losses at the surface are reduced.

The presence of metallic Ga in the course of annealing does not lead to any changes in the PL spectrum for the powder in which the sizes *d* the particles are smaller than 40 μm (Fig. 1, curve *3*). The PL spectra of the annealed samples are nearly identical. It has previously been shown [4] that, if there are no extraneous atoms that can affect the diffusion rate and the rate of replacement of Zn by Ga in ZnS, the introduction of Ga atoms into the ZnS bulk is almost absent.

The behavior of the ZnS-powder fraction in which the sizes of the particles are larger than 40 μm is radically different. For the powder particles agglomerated into clusters in which the sizes exceed 40 μm, the presence of metallic Ga in the course of annealing leads to significant changes in the PL spectrum (Fig. 2, curve *3*). This spectrum consists of a complex band in the blue-green spectral region whose peak is located at λ_{max} = 505 nm. In addition, the shape of the short-wavelength wing of the PL spectrum indicates that there is at least one other single band in the region of ~470 nm. It was previously shown in [1, 8–10] that the band with λ_{max} = 470 nm could be attributed to the presence of Ga in ZnS.

In addition, efficient electroluminescence is a characteristic of ZnS powder, annealed in the presence of metallic Ga, in which the sizes of the particles are ≥40 μm. The EL spectrum of this powder (Fig. 2, curve *3*) consists of a band with a peak at λ_{max} = 500 nm and a half-width of 75 nm.

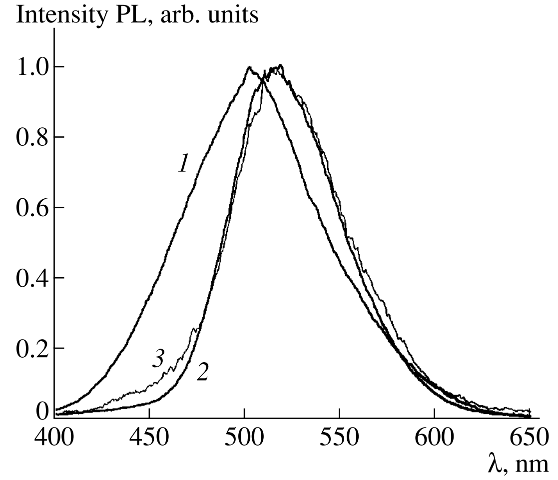

Fig. 1. Photoluminescence spectra of (*1*) the initial (unannealed) ZnS powder, (*2*) the annealed ZnS powder, and (*3*) the ZnS powder annealed in the presence of Ga (the powder in which the sizes of the particles were no larger than 40 μm). The curves are normalized to the maximum.

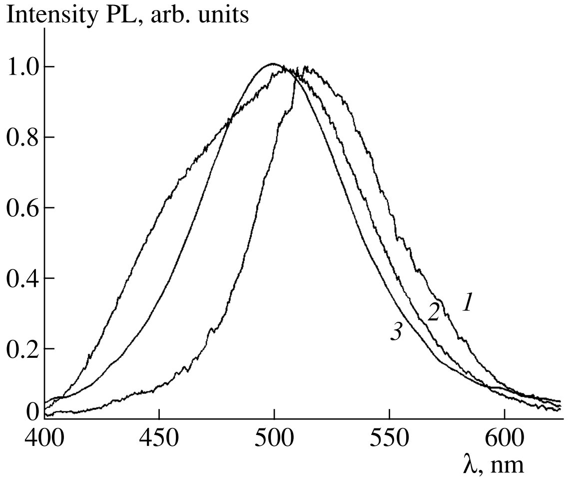

Fig. 2. Luminescence spectra of the ZnS powder annealed in the presence of Ga for the powders in which the sizes of the particles were (*1*) no larger and (*2, 3*) larger than 40 μm. Curves *1* and *2* represent the photoluminescence spectrum and curve *3* represents the electroluminescence spectrum. The curves are normalized to the maximum.

4. DISCUSSION

Analysis of the obtained results showed that the fractions of the ZnS powder doped thermally with Ga in which *d* ≥ 40 μm and *d* < 40 μm exhibited considerably different luminescent properties. For example, the PL spectrum of the ZnS powder with *d* ≥ 40 μm included a band peaked at λ_{max} = 470 μm, caused by the presence of Ga in ZnS; the peak of this spectrum shifted by 10 nm to shorter wavelengths with respect to the PL spectrum of the powder with *d* < 40 μm. In addition, electroluminescence emission was not observed for the

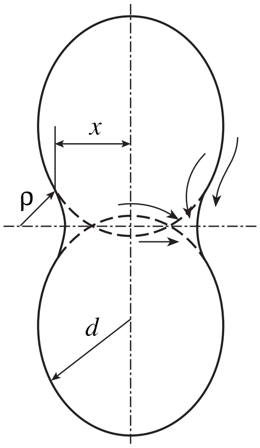

Fig. 3. A model of two agglomerating spheres (the possible diffusion directions are indicated).

ZnS powder that was doped thermally with Ga and had $d < 40$ μm, whereas the fraction of this powder that had $d \geq 40$ μm exhibited electroluminescence with an intensity sufficient for reliable detection (Fig. 2, curve *3*). We were unable to find any data in previous publications on the EL of zinc sulfide where Ga acted as a coactivator. In this case, Ga probably acts as a coactivator for the uncontrolled impurities (Cu, Mn, Al) or intrinsic ZnS defects that are responsible for self-activated emission.

Thus, the above reasoning makes it possible to conclude that the agglomeration of separate particles of the ZnS powder in the course of the annealing of this powder at 800°C in the presence of Ga gives rise to conditions under which Ga atoms penetrate into the ZnS bulk, where some of these atoms then occupy the Zn sites (Ga_{Zn}).

As was mentioned above, the pressing of the ZnS powder into pellets and their subsequent annealing at a temperature of 800°C leads to the agglomeration of ~40% of the ZnS volume into particles with $d \geq 40$ μm. The fact that some of the powder's particles agglomerate into larger clusters at a temperature that is several times lower than the melting point is well known and has been described in a number of publications [11, 12]. In the case under consideration, agglomeration occurs at a temperature that is lower than the ZnS melting point (T_m = 1850°C) [13] by a factor of 2.3.

The main driving force for the process of agglomeration (agglomeration in the solid phase is also referred to as densification) consists in a decrease in the free energy of the system, mainly of the system's surface energy. The surface tension (capillary forces) gives rise to stresses in a solid. These stresses depend on the surface curvature according to the Laplace equation; i.e.,

$$\sigma = \gamma(-1/\rho + 1/x), \qquad (1)$$

where σ is the stress in the contact neck, γ is the surface tension, ρ is the curvature radius in the vicinity of the neck, and x is the neck radius. Equation (1) can be used to describe the process of agglomeration in a two-sphere model (Fig. 3). The material shifts to the neck region via the volume, grain-boundary, and surface diffusion that corresponds to either the Herring–Nabarro or Coble creep. This mechanism becomes the most important in the agglomeration of the powder's particles in the absence of an external pressure [12]. The initial stage of agglomeration, which is due to the volume diffusion, can be described by the equation

$$x^2/a^2 = (40\gamma\Omega D_V/RT)t, \quad (x^5/d) = Kt, \qquad (2)$$

where d is the radius of the sphere, D_V is the volume-diffusion coefficient, Ω is the atomic volume, T is temperature, and t is time. Equation (2) makes it possible to draw an important conclusion: the agglomeration rate increases as temperature increases and the particle size decreases. In the first approximation, we may assume that, in the case of zinc sulfide, the particles with a diameter smaller than 20 μm are actively agglomerated in the solid phase at $T \geq 850$°C if the effect of pressing is disregarded.

In addition, the annealing gives rise to a thermal deformation of the surface of the powder's particles, which leads to surface destruction and is accompanied by the generation of an excess concentration of vacancies and interstitial atoms and to appearance of their clusters; as a result, a thin surface layer becomes preferentially thermally disordered [14].

All the aforementioned phenomena stimulate the agglomeration of separate particles, although these phenomena do not lead to the agglomeration of the entire mass of the material into a combined "porous" conglomerate. In our opinion, this behavior is caused by the fact that the crystallographic axes of the contacting faces of the crystallites in the powder are misoriented with respect to each other. Therefore, a good match between the lattices of the crystallites is not attained. Consequently, the agglomeration of crystallites over the entire volume of the powder subjected to annealing proceeds differently, and most of the powder's crystallites are not agglomerated. It is worth noting that this circumstance leads to a defect-rich agglomeration boundary.

Thus, taking into account both the data [4] that are indicative of the physical adsorption of Ga at the surface of powder's particles, but without any subsequent active penetration of Ga into the particle's volume during ZnS annealing in the presence of Ga, and the processes accompanying the agglomeration of the particles, we can suggest the main factors that allow the Ga atoms to penetrate easily into the ZnS bulk when the powder is pressed into pellets.

The first factor is related to the fact that Ga atoms, after being trapped at the surface, are found within newly formed (larger) 40-μm particles in the course of the agglomeration of the powder's particles. This behavior is caused by the surface diffusion of the main material into the neck region; as a result, Ga is found to be under the corresponding layer (see Fig. 3). The second factor is related to the fact that the diffusion coefficient of the impurity increases as the size of the crystallites increases, as was shown in [15]. The third factor is related to the fact that the diffusion over the grain boundaries occurs at a higher rate than that in the crystals' bulk since the proper crystal structure is disrupted in the regions that include structural defects in the vicinity of the grain boundaries (dislocations and stacking faults).

Thus, the results reported in this paper indicate that annealing at temperatures corresponding to the agglomeration of ZnS particles in the solid phase, after ZnS has been pressed into pellets in the presence of Ga, is conducive to the active penetration of Ga into the ZnS bulk. We would like to emphasize that, in the case under consideration, we used a minimal number of materials in the course of introducing Ga into the ZnS matrix; as a result, we minimized the amount of extraneous impurities (such as S, Ga, and Zn; uncontrolled impurities; and impurities coming from the residual atmosphere) that accompanied the technological process of doping. In other thermal methods for doping ZnS with Ga, either Ga salts or Ga in combination with materials that increase the diffusion rate of Ga from the surface into the ZnS matrix were used; i.e., these materials acted as catalysts [1, 4, 8–10].

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Translated by A. Spitsyn