

Influence of Preparative Conditions on Optical and Morfo-structural Properties of Zinc Sulphide Thin Films

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Zinc sulphide thin films were deposited on optical glass platelets, from chemical bath containing variable amounts of thiourea, zinc acetate, ammonia and sodium citrate. The mono and multilayer technique was used in order to prepare ZnS/glass/ZnS structures with variable film thickness. The films, as were prepared and after annealing, were investigated by UV-VIS absorption/reflection spectroscopy, photoluminescence spectroscopy, scanning electron microscopy and X-ray diffraction. The optical and morfo-structural characteristics of zinc sulphide layers are strongly influenced by deposition technique reagent concentrations as well as by the annealing regime and doping conditions.

Keywords: Zinc sulphide, metal chalcogenide, chemical bath deposition, thin films

Zinc sulphide (ZnS) is an interesting semiconductor with a wide band gap, which attracts much attention because of its interesting optoelectronic properties. There are a diverse range of applications for ZnS thin films such as photovoltaics, electro luminescent displays and other optoelectronic devices [1-4].

The techniques, which have been adopted, for the preparation of metal chalcogenide (ZnS, CdS) films are molecular beam epitaxy [5], sputtering [6], pulsed-laser deposition (PLD)[7], metal-organic chemical vapor deposition (MOCVD)[8] chemical bath deposition (CBD) or electrodeposition [9-11]. The chemical bath deposition (CBD) is a very attractive method for producing ZnS thin films, due to the possibility of large area deposition at low cost, which has been successfully used for deposition of other sulphides and selenides i.e CdS, ZnSe, MnS, ZnCdS etc. Chemical bath deposition process is based on the controlled release of the metal ions (Zn^{2+}) and chalcogenide ions (S^{2-}) in the presence of ammonia and chelating agents with their subsequent interaction to form the zinc sulphide thin layer onto the substrate.

In this paper, the effects of the growing conditions and the annealing regime on optical and morfo-structural properties of ZnS thin films are discussed. The special optical properties *i.e.* photoluminescence of some doped ZnS thin films were also investigated.

Experimental part

ZnS thin films have been grown on 3 . 4.5 . 1 cm² optical glass substrates by CBD technique. The deposition of ZnS was carried out from a mixture of zinc acetate (0.1M) as the zinc ion source, thiourea as the sulphur source, NH₃ aqueous solution and sodium citrate. Sodium citrate was added as a complexing agent and ammonia was used to adjust the pH value. The bath temperature during the deposition was maintained in the range of 82-86°C and the pH of the solution within the values of 9.5-10.5. The details of experimental technique have been described in our previous works [12-14]. Thick samples were produced by monolayer technique (continuous deposition) and multilayer technique (successive depositions).

Several samples series were prepared as follows:

- Series A: multilayer; 2 . 1h; $[Zn^{2+}]:[Cyt^3]=1:4 \div 1:0.5$; Samples F1.3; F2.1; F3.2; F4.3; F5.3; F6.2; F7.2 ;
- Series B: monolayer; 1 . 2h; $[Zn^{2+}]: [Cyt^3]=1:4 \div 1:0.5$; Samples F1.6; F2.4; F3.4; F4.4; F5.6; F6.6; F7.4.
- Series C: monolayer; 1 . 4h; $[Zn^{2+}]: [Cyt^3] =1:3$; Samples: F8.8; F17.1.
- Series D: multilayer; 4 . 1h; $[Zn^{2+}]:[Cyt^3]=1:3$; Samples: F9.2; F9.3; F10.3; F22.4; F28.3; F36.5.

Some of the samples were annealed either in air (550°C) or under nitrogen atmosphere (at 500°C). In order to develop luminescent properties of ZnS thin films, Cu and/or Mn-salts were introduced into the chemical bath and the annealing stage was performed at 500°C, in nitrogen inert atmosphere. Film thickness (h) was evaluated by the micro-weighing method [15]. The optical properties of ZnS thin films were evaluated with an UNICAM Spectrometer UV4. A Perkin Elmer 204 Fluorescence Spectrofotometer was used to investigate photoluminescence characteristics. Crystalline structure was determined with a standard DRON-3M Diffractometer using the filtered $K\alpha$ emission of copper. ZnS/glass/ZnS heterostructures have been analyzed as grown and also after thermal treatment in air and nitrogen atmosphere.

Results and discussion

The preparation of ZnS thin films by CBD was based on the reaction between zinc acetate $Zn(CH_3COO)_2$ and thiourea $(NH_2)_2CS$ solutions, in a basic medium using sodium citrate solution as a complexing agent. ZnS thin films were grown (1) by mono- and multilayer technique, from chemical bath with the following composition: $[zinc\ acetate] = 15 \cdot 10^{-3} M$; $[sodium\ citrate] = 7.5 \cdot 10^{-3} \div 60 \cdot 10^{-3} M$; $[ammonia] = 300 \cdot 10^{-3} M$; $[thiourea] = 150 \cdot 10^{-3} M$.

Under the above-mentioned conditions, adherent and homogeneous ZnS thin films were grown on both sides of the glass substrates to give the ZnS/glass/ZnS heterostructures. Some ZnS /glass heterostructures were obtained by the removal of ZnS films from one side of the glass.

The formation of the ZnS thin films takes place either in the bulk of the solution due to the spontaneous ZnS precipitation, by a homogeneous reaction, or at the surfaces

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of the substrate leading to the formation of the film, by a heterogeneous reaction. The general reaction involved in the deposition process was:



The influence of the concentration of the complexing agent (sodium citrate) on the ZnS films thickness has been investigated at constant zinc acetate and thiourea concentrations. The molar ratio between Zn^{2+} and $\text{C}_6\text{H}_5\text{O}_7^{3-}$ (abbreviated as Cyt^{3-}) species was varied between 1.0: 0.5 and 1.0: 4.0. The dependence of ZnS film thickness on sodium citrate concentration is illustrated in figure 1. For the same total deposition time, one can note that monolayer deposited ZnS thin films have smaller thickness than those of multilayer deposited ones.

Film transparency decreases with the increase of its thickness, as found previously [16].

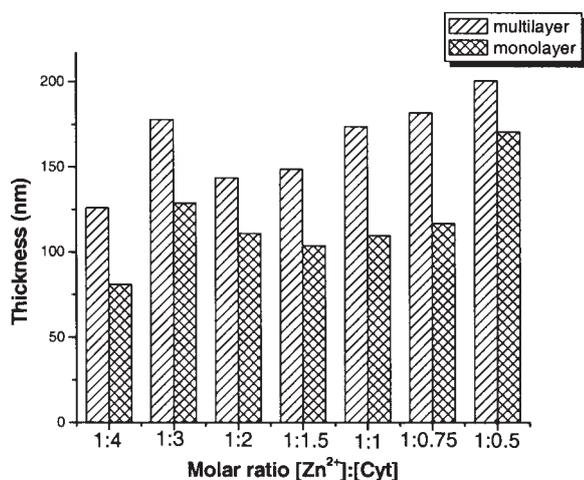


Fig. 1. Variation of films thickness with different $[\text{Zn}^{2+}]:[\text{Cyt}^{3-}]$ ratios

The concentration of complexing agent influences both the growing rate and the film quality. Under employed experimental conditions, two categories of samples could be prepared namely adherent and homogeneous films at high Na-citrate concentration ($[\text{Zn}^{2+}]:[\text{Cyt}^{3-}] = 1:2 \div 1:4$) and powdery and less adherent films at relatively low citrate concentration ($[\text{Zn}^{2+}]:[\text{Cyt}^{3-}] = 1:0.5 \div 1:1.5$).

Figure 2 presents the comparative transmittance spectra of some ZnS/glass/ZnS heterostructures grown by multi- and monolayer technique at different molar ratio $[\text{Zn}^{2+}]:[\text{Cyt}^{3-}]$.

The optical transmittance of ZnS thin films is strongly influenced by the preparation conditions of ZnS/glass/ZnS heterostructures. In both cases, the transmittance of films grown by multilayer technique is smaller than that one of films grown by monolayer technique. Moreover, the optical homogeneity of the films prepared in baths with relatively low citrate concentration is poor.

The thickness values and the transmittance spectra suggest that the best films quality could be obtained in bath with the ratio $[\text{Zn}^{2+}]:[\text{Cyt}^{3-}] = 1:3$. At this reagent molar ratio, the films exhibit more than 70% transmittance. The optimal deposition bath, considering all ingredients, corresponds to the reagent ratio of: $[\text{Zn}^{2+}]:[\text{Cyt}^{3-}]:[\text{NH}_3]:[\text{thiourea}] = 1:3:20:10$. These conditions were considered as standard.

The reflectance spectra of ZnS/glass heterostructures obtained at different sodium citrate concentrations were registered in order to evaluate the ZnS film optical quality (fig. 3). The spectra registered at 0° incidence indicate the

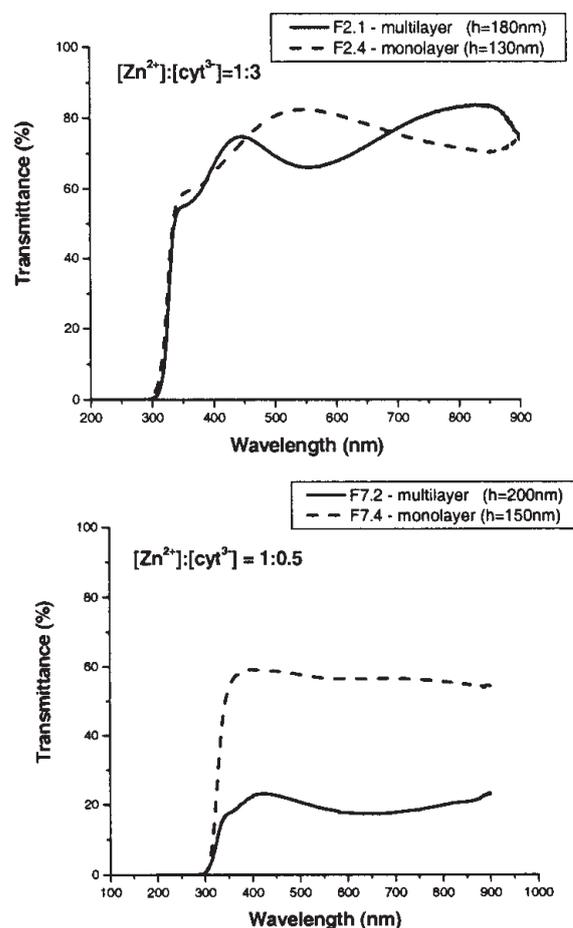


Fig. 2. Comparative transmittance spectra of some ZnS/glass/ZnS heterostructures grown by multi- and monolayer technique

diffuse reflection of the films, whereas the spectra obtained at 8° incidence of the visible light illustrate both the specular and diffuse reflection properties of the investigated structure. The specular reflectance of samples, evaluated as the difference between the reflections measured at 8° and 0° incidence, decreases as the sodium citrate concentrations decreases. One can note a strong specular reflection properties of the ZnS films obtained in the standard conditions ($[\text{Zn}^{2+}]:[\text{Cyt}^{3-}] = 1:3$).

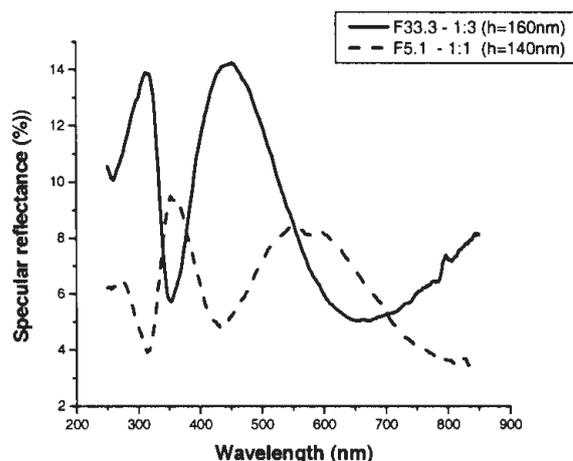


Fig. 3. Specular reflectance of ZnS/glass heterostructures prepared by multilayer technique, using different $[\text{Zn}^{2+}]:[\text{Cyt}^{3-}]$ ratios

Information on surface structure and morphology of the films were obtained by means of SEM investigations. A series of SEM images were performed to characterize and compare the surface structure and morphology of the films. Figure 4 shows the SEM images of the surface of some ZnS/glass/ZnS heterostructures obtained under different

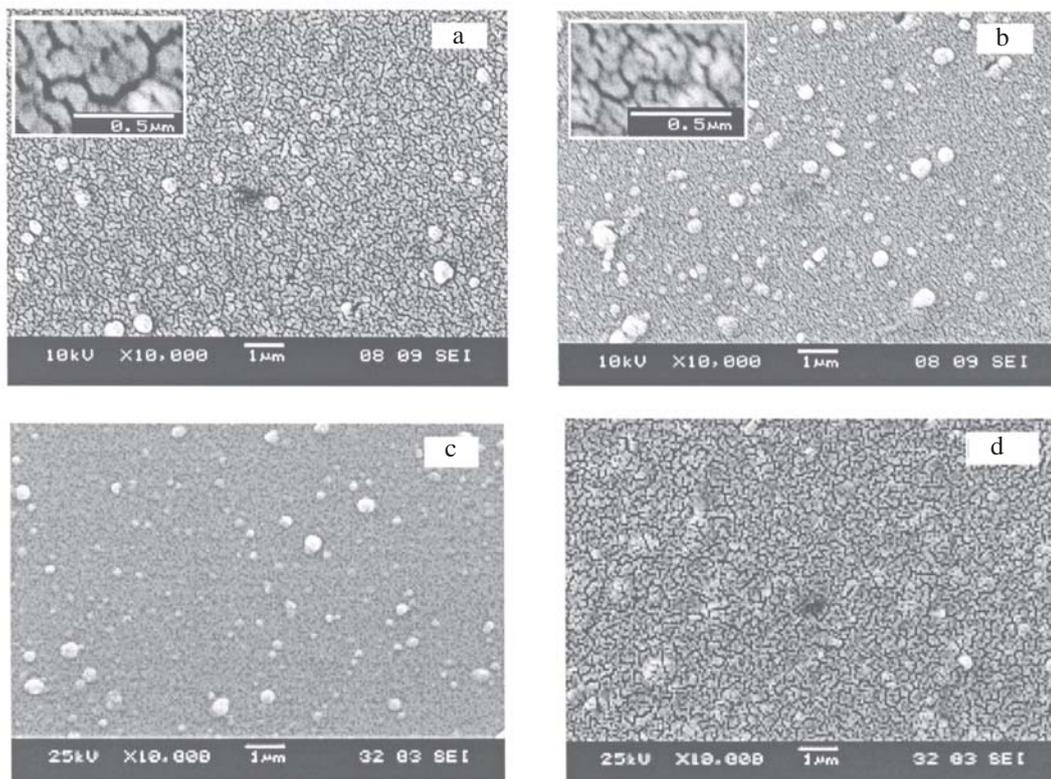


Fig. 4. SEM images of some ZnS/glass/ZnS heterostructures prepared using different reagent ratios and deposition techniques. a: monolayer, $[Zn^{2+}]:[Cyt^3]=1:2$; b: monolayer, $[Zn^{2+}]:[Cyt^3] = 1: 1.5$; c: monolayer, $[Zn^{2+}]:[Cyt^3] = 1: 3$; d: multilayer, $[Zn^{2+}]:[Cyt^3] = 1: 3$

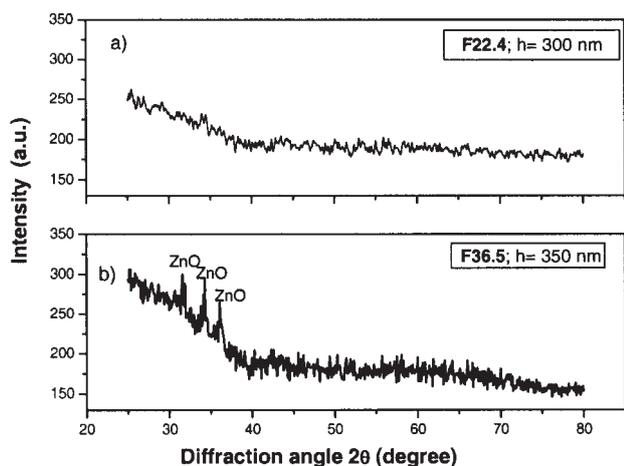


Fig. 5. XRD pattern for the as deposited ZnS films annealed in nitrogen (a) and air (b)

growing conditions: a) monolayer technique, from bath with different sodium citrate concentrations (fig. 4a, b) and b) monolayer (fig. 4c) and multilayer (fig. 4d) technique. SEM micrographs reveal that the films grown by monolayer technique show quite smooth surfaces with few spherical blobs scattered over them.

In order to consolidate the CBD thin films, an annealing treatment under nitrogen atmosphere or air was performed. The crystallographic properties of annealed ZnS thin films have been investigated by XRD technique. Figure 5 shows XRD diffractograms for as deposited CBD-ZnS films annealed under inert atmosphere (a) and respectively, in air (b). The X-ray diffractograms of the heat-treated ZnS thin films are typical for the non-crystalline structures. But, for the air-annealed ZnS thin film, additional diffraction lines of ZnO can be noticed in the XRD patterns. Moreover, the shape of the experimental X-ray scattering curve of the

nitrogen annealed ZnS thin film suggests a more pronounced structural disorder in this system.

In the non-crystalline solids like amorphous chalcogenides there is a local order, a short-range order, characterized only for the first coordination spheres of the component atoms, i.e. at the distances at which the interatomic forces are acting. The local order in amorphous and crystalline compounds of the same composition has both similarities and differences. The differences are assigned to the loss of long-range order, to the deviation from a perfect crystalline structure. The atoms arrangement in the first coordination sphere is determined by the chemical composition and peculiarities of chemical bonds and generates the local order around them that is very important to depict the non-crystalline systems. There are also amorphous systems wherein, the local structure is extended at more than some coordination spheres imposing a middle or intermediate range order [17].

The physical properties of non-crystalline systems can be explained assuming that their disordered structure is obtained by interconnection of structural units depending on the type and amount of component atoms entering in the considered system. Short-range order of amorphous thin film of zinc sulphide system was investigated by analyzing the atomic radial distribution function obtained from X ray scattering data [18] using a PEDX program [19].

The real space distance corresponding to the maxima determined from the data obtained in this study may be compared with results reported for other similar systems and allow to identify the atom pairs that are orderly disposed in the investigated system. They are summarised in table 1. Inspecting the data from the analysis of atom pair correlation function g_l obtained for the ZnS as grown (AG) thin film, one remarks the occurrence of the maxima as a first coordination formation, well composed at a distance of 2.77 Å and a second maxima corresponding to

Table 1
ATOM PAIRS THAT ARE ORDERLY DISPOSED IN ZINC CHALCOGENIDE SYSTEM, IDENTIFIED FROM THE ANALYSIS OF ATOM PAIRS CORRELATION FUNCTION g_l

| Coordination sphere | Atom pairs | Inter-atomic distance in ZnS – hexagonal [Å] | Space distance corresponding to the maxima of the atom pairs correlation function [Å] |
|---------------------|------------|--|---|
| I | Zn – S | 2.56 | 2.77 |
| | Zn – Zn | 2.86 | |
| II | Zn – Zn | 3.04 | 3.07 |
| III | Zn – Zn | 3.82 | 3.59 |
| | | | 4.02 |

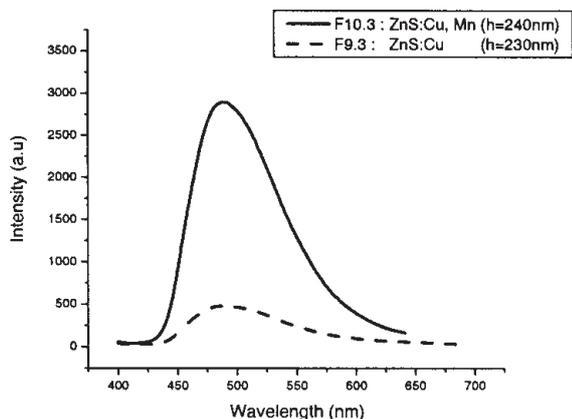


Fig. 6. Photoluminescence spectra of ZnS/glass/ZnS heterostructures prepared with different activators

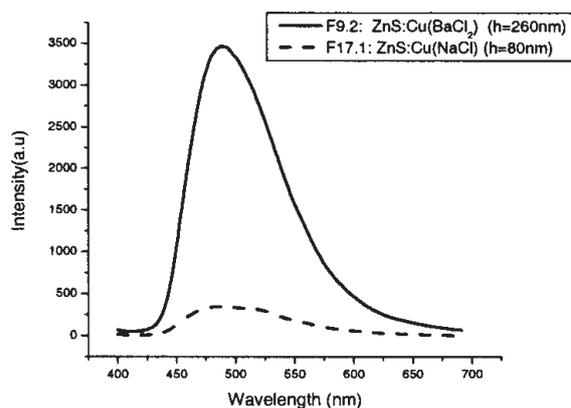


Fig. 7. Photoluminescence spectra of ZnS/glass/ZnS heterostructures prepared with different co-activator supplier

Table 2
PHOTOLUMINESCENCE (PL) CHARACTERISTICS OF SOME ZnS/GLASS/ZnS HETEROSTRUCTURES

| Sample code | Heterostructure | PL colour | PL characteristics | |
|-------------|--|-----------|--------------------|---------------------|
| | | | I em (a.u) | λ_{pk} (nm) |
| F9.2 | ZnS(Cu, BaCl ₂)/glass/ ZnS(Cu, BaCl ₂) | Green | 3460 | 489 |
| F9.3 | ZnS(Cu)/glass/ ZnS(Cu) | Green | 480 | 490 |
| F10.3 | ZnS(Cu, Mn)/glass/ ZnS(Cu, Mn) | Blue | 2895 | 488 |
| F17.1 | ZnS(Cu, NaCl)/glass/ ZnS(Cu, NaCl) | Green | 344 | 487 |

the 3.04 Å. The occurrence of these maxima suggests the formation of a local structure based on the ZnS hexagonal arrangement like in the ZnS hexagonal structure (SG P63mc. $A=3.82$ Å, $b=3.82$ Å, $c=6.26$ Å, - PDF file 5-492).

XRD patterns suggest that the recommended treatment to prepare luminescent ZnS thin films are under nitrogen atmosphere. On the basis of these results luminescent ZnS thin films were prepared by direct doping conditions. It is known that the light emitting properties of ZnS thin films are highly influenced by the annealing regime as well as doping conditions [16, 20].

The photoluminescence (PL) spectra of some luminescent ZnS/glass/ZnS heterostructures prepared by direct doping are depicted in figure 6 and figure 7 and the main PL characteristics are summarized in table 2.

All the samples show the blue-green emission around 487-490nm. ZnS (Cu, BaCl₂)/glass/ ZnS(Cu, BaCl₂) heterostructure presents the strongest emission band, as shown in table 2. The influence of different activators on the photoluminescence (PL) spectra of ZnS/glass/ZnS heterostructures is illustrated in figure 6.

The PL spectrum of ZnS (Cu)/glass/ZnS (Cu) heterostructures exhibits a less intense emission band centred at about 490 nm. The positions of that band illustrate the composite nature of the spectrum that clearly contains self-activated and Cu-emission centres.

ZnS(Cu,Mn)/glass/ZnS (Cu,Mn) heterostructures, obtained by direct doping regime, show a strong blue emission band (~488 nm) that could be associated with the activator presence (Cu-or Mn-emission centres).

The influence of co-activator source on the photoluminescence emission of ZnS/glass/ZnS heterostructures is illustrated in figure 7. The addition of NaCl into the chemical bath during the growing process exhibits no influence the luminescent properties of the heterostructure. On the contrary, the use of BaCl₂ and its presence during the annealing stage strongly contributes to the formation of Cu-emission centres and improves the photoluminescence of the as prepared films.

Conclusions

High quality zinc sulphide thin films were prepared by chemical bath deposition onto optical glass platelets using zinc acetate– sodium citrate – ammonia – thiourea system, using mono- and multilayer deposition technique. The concentration of chelating agent (sodium citrate) proved to be important for the deposition of uniform and adherent ZnS films, with controllable thickness.

UV-Vis investigation illustrated that the increase of films obtained by multilayer deposition technique are more optical homogeneous.

Surface film morphology is different for films obtained from bath with different sodium citrate amounts and different deposition technique. Both films as -grown and N₂ annealed film are non-crystalline materials. ZnS film annealed in the air contains also ZnO as secondary phase. Additional XRD investigations suggest the formation of a local structure based on the ZnS hexagonal arrangement.

XRD patterns suggest that the recommended treatment is under nitrogen inert atmosphere.

The photoluminescence measurements revealed as formed films show the ability to develop light emitting properties when the chemical bath contains some metallic doping ions (activator supplier) and chloride containing salts (co-activator supplier).

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