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Structural investigations of annealed ZnS:Cu, Ga film phosphors

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Abstract. X-ray and atomic force microscopy techniques were used for investigations of crystalline structure and nano-morphology of ZnS:Cu thin films. The films were deposited by electron beam evaporation on substrates of various types (glass, $BaTiO_3$, silicon). New non-vacuum method of annealing was applied for improvement electro-physical parameters of ZnS:Cu based thin film electroluminescent devices. The annealing was carried out at the temperature of 850 °C. Ga co-doping was applied for the same structures in the course of the annealing process. It was shown that recrystallization process at annealing leads to improvement of ZnS:Cu films structural perfection without changes of crystal structure. This improvement provides tenfold increase of photo- and electroluminescence brightness and decrease of threshold voltage down to 10 V, as well as enhancement of device stability against degradation.

Keywords: X-ray, AFM, ZnS:Cu, phosphor thin films, annealing, electroluminescence.

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1. Introduction

Polycrystalline films based on A^2B^6 compounds are actively applied in optoelectronics recently, in particular for making high resolution colour electroluminescent and cathodoluminescent displays of various types, field emission displays, etc.

Great attention is paid to ZnS:Cu thin films that can be considered as emitters of green and dark blue colors. But the alternating-current ZnS:Cu thin-film electroluminescent structures obtained by known vacuum methods degrade much faster than ZnS:Mn films (see, for example [1]). Only films with stable electroluminescent (EL) and photoluminescent (PL) properties could be employed in industrial manufacturing. Stability of thin films against degradation is determined by their structural perfection. It was shown recently [2,3] that films deposited by electron beam evaporation (EBE) method and annealed at high temperatures (800-900 °C) are characterized by slower (1-2 orders of magnitude) degradation of an active layer. Besides, the additional Ga doping improves intensity of PL and EL considerably.

A new non-vacuum method of phosphor films doping by certain impurities was developed [4]. A method consists in deposition of certain dopant amount onto a structure at atmospheric pressure and at the temperature characteristic to the dopant source. The composition of atmosphere for doping is specially selected for obtaining the film with required stoichiometry. The method was applied for Ga co-doping of ZnS:Cu films simultaneously with high temperature annealing.

The effect of annealing conditions and type of substrate on ZnS:Cu films structure was the aim of our investigations.

2. Experiment

The ZnS:Cu films were deposited on various substrates ($BaTiO_3$ ceramics, glass and silicon) by EBE method from ZnS:Cu target. The Cu concentration in a target was 0.25 %. Thickness of films varied from 0.6 up to 8.0 μm. Temperature of a substrate at deposition in all cases was about 150 °C.

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Thin-film structures were annealed after deposition in S_2-rich atmosphere at temperature of 850 °C for one hour. Gallium doping was carried out simultaneously with annealing at atmospheric pressure using new method [4]. The Ga vapor was inserted in annealing atmosphere from sources with various distribution and concentration of gallium.

For observation of EL, the device structure schematically shown in Fig. 1 was made. The metal electrode and dielectric $BaTiO_3$ (thickness of 40 μm) were deposited upon basic substrate using special technology [5]. Then, the ZnS:Cu film was deposited by EBE. The upper semitransparent gold electrode was deposited by thermal evaporation method after annealing and gallium doping.

The structural and luminescent characteristics of obtained films were explored by X-ray diffraction methods, atomic force microscopy (AFM) and optical methods, namely:

(i) X-ray diffraction patterns analysis for crystalline structure determination. Patterns were recorded in symmetric and grazing incidence geometries using Cu $K_{\alpha 1,\alpha 2}$ - radiation;
(ii) diffraction peak position and line-broadening analyses for determination of strains and grain sizes;
(iii) AFM for study of morphology surface;
(iv) investigations of EL excited by a sine voltage with frequency of 1 kHz.

3. Results

The analysis of X-ray patterns shows that ZnS in a target before EBE was in the form a polycrystal with wurtzite structure (Fig. 2), and after EBE for ZnS in a target only sphalerite structure was observed. All deposited ZnS:Cu films have sphalerite structure with preferable orientation in <111> direction independently on the type of films structure and thickness. Annealing (both without and with gallium vapor) does not transform the type of structure of films (Fig. 2). It must be emphasized that ZnO phase was not detected despite the annealing was carried out at atmospheric pressure and at oxygen presence. In the films after annealing with Ga co-doping, a deviation from stoichiometric ZnS compound was not detected also by energy-dispersion microprobe analysis at measurements accuracy to 0.05%.

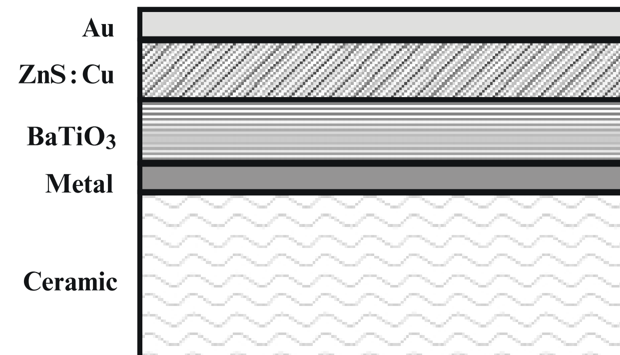


Fig. 1. The scheme of the thin-film alternating-current EL device structure.

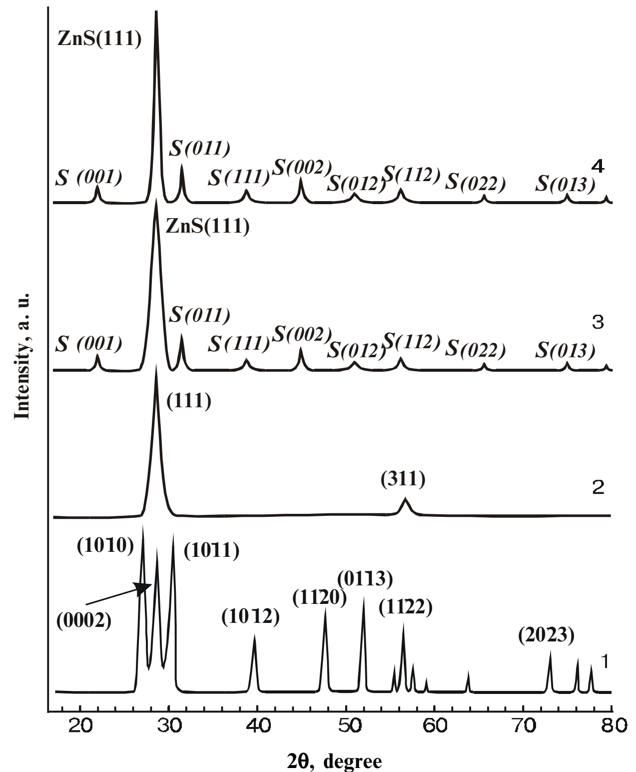


Fig. 2. X-ray patterns of : ZnS:Cu target before evaporation (1); ZnS:Cu film on glass before annealing (2); ZnS:Cu film on $BaTiO_3$ before annealing (3); ZnS:Cu film on $BaTiO_3$ after annealing (4) (S denotes peaks from $BaTiO_3$ substrate).

There is only one strong peak from ZnS film on X-ray pattern, thereby a quantitative estimation of grain sizes according to line-broadening analysis was done only approximately, because it is impossible to separate effects of strains and sizes on line broadening [6]. Besides, it was taken into account that the observed line profile is a convolution of both instrumental and specimen broadening of the diffraction line with K_α-doublet.

For subsequent line-broadening analysis, it is necessary to obtain the parameters of pure physically broadened line profile. So, deconvolution approach where the physically broadened line profile was unfolded from the observed profile was done using the previously determined instrumental profile and approximation with some analytic function line profile. From pure physical line profile the K_α-doublet peaks position and integral breadths of lines were determined. An average size of crystallites D was approximately calculated from the integral breadth of $K_{\alpha 1}$ line using Sherrer equation [7, 8]:

$$D = \frac{1.155\lambda}{H \cos\theta}, \quad (1)$$

where θ is a Bragg angle, λ is a wavelength and H is integral breadth. The results of evaluations are shown in Table 1.

Table 1. Sizes of grains and strains determined for as-deposited films with thickness of 8 μm.

Sample	$\Delta(2\theta_{K\alpha1,2})$, degrees	Film Strain, GPa	H, radians	D, nm
$ZnS/BaTiO_3$	0.84	4.55	0. 00513	31
ZnS/glass	0.79	6.09	0. 00973	16
ZnS/silicon	0.62	0.49	0. 00378	42

The quantitative estimations of residual strains and their relaxation were performed according to the Stouney equation [9]. Curvature radii were obtained from analysis of distance between peaks of $K_{\alpha1,2}$-doublet $\Delta(2\Delta_{K\alpha1,2})$ [10,11].

As it could be seen from the Table 1, both sizes of grains and value of strains in films depend on a type of substrate. Average size of crystalline grains in a thick film is the largest one in the case of a single crystal silicon substrate and the smallest in the case of amorphous (glass) ones. Despite the largest value of film grain sizes and small residual strains on silicon substrate, which would make silicon to be an optimum substrate, the difference in coefficients of thermal expansion is significantly higher in comparison with structures on glass and ceramics. It leads to exfoliation of a ZnS film from a substrate after annealing. Therefore, the silicon substrate cannot be used for ZnS device structures manufactured by this method.

The values of parameters, which are shown in Table 1, after annealing and gallium doping became close to the obtained values for ZnS powder according to instrumental broadening of the diffraction lines. The value of integral breadth decreases to the instrumental integral breadth (without broadening caused by presence of mosaic blocks and strains) and distance between K_α-doublet approached to simulated value for flat substrate. It enables to assume that the average size of crystalline grains increased considerably (~ 1 μm) and process of strains relaxation took place.

AFM investigations of ZnS surface showed that island growth mechanism is realized during deposition and the type of substrate as well as further treatment essentially influence on film morphology, in particular, on the sizes of grains.

Different origination and grains sizes were observed during films growth on various substrates. For initial stage of growth the smallest grains size and the most homogeneous sizes are observed on glass substrate, in contrast to a silicon substrate, where grains are largest with several distinguishing sizes of grains (Fig. 3). The films with thickness of some tenths of micron have average size of grains equal to 250 nm for $BaTiO_3$ substrate, 120 nm for a glass and 300 nm for a silicon substrate. If the film thickness of 8 μm has been reached, their surface becomes so nonuniform and complicated for analysis (independently from substrate) that it is possible to allocate only separate blocks, which grown in processes of grains coagulation and achieved sizes of 0.7 to 1.0 μm.

The shown results indicate that the most perspective material for our device structures is polycrystalline $BaTiO_3$. Its surface consists from grains with sizes of 7-9 μm and does not change at annealing and Ga co-doping. The ZnS:Cu films deposited on $BaTiO_3$ have small size grains with fuzzy boundaries. The grain sizes are increased (~ 600 nm) after annealing without gallium doping. Their boundaries become sharper, but subgrain structure (~ 120 nm) still remains. After thermal annealing with a simultaneous Ga doping, the sizes of grains are larger (700-1000 nm), and the surface become smooth, no subgrains are observed (Fig. 4).

The essential difference in ZnS:Cu surface morphology was observed in dependence on the used Ga source (a plate with homogeneous Ga distribution or powder with nonuniform Ga distribution). As could be seen from Fig. 5a, the grains have smooth surface and legible boundaries in the case of source with homogeneous gallium distribution, and in the case of the nonuniform one (Fig. 5b) there is a significant dispersion in grain sizes. The largest size grains are localized mainly on the substrate elevations. In our opinion, such concentration of large size grains takes place in the area of Ga enrichment. AFM artifacts presented near these areas can testify in favour of such assumption. The origin of artifacts can be the Ga drops on ZnS film surface in such areas where character of tip-sample interaction changes, in particular, due to the adhesion and frictional force variety [12]. In this case, it is possible to separate contributions of annealing only and annealing with Ga co-doping, although the mechanism of such strong influence of Ga co-doping on grain sizes growth is unclear so far.

PL and EL investigations show that optical properties of ZnS:Cu films appreciably depend on post-deposition processing parameters (annealing and Ga co-doping). As-deposited films have weak PL intensity. The PL luminosity is increased by the factor of five after annealing at 850 °C and hundredfold after annealing with a simultaneous Ga doping. The EL luminosity after annealing increased by three times in comparison with that in initial films. Luminosity of EL increased essentially after annealing with simultaneous Ga doping, as well as threshold voltage has reduced from 110 V down to 10 V.

According to obtained results about crystalline structure after annealing both without and with Ga co-doping from different sources, it is possible to assume that at this process Ga acts not only as co-dopant for improvement luminescent properties, but as activator of collecting and secondary recrystallization processes, which facilitate a coarse-grain formation. Diffusing Ga atoms in a depth of film gather at subgrain boundaries and accelerate the grain growth process, when big grains grows at the cost of small one with decreasing surface energy [13]. Presence of some liquid phase (Ga in our case with melting point 29.7 °C) essentially accelerates all mass-transfer processes during annealing, and as a consequence, at used annealing temperatures an intensive magnification of grain sizes occurs.

ZnS:Cu/Glass

ZnS:Cu/Si

I II III

Grain number

Grain size, nm

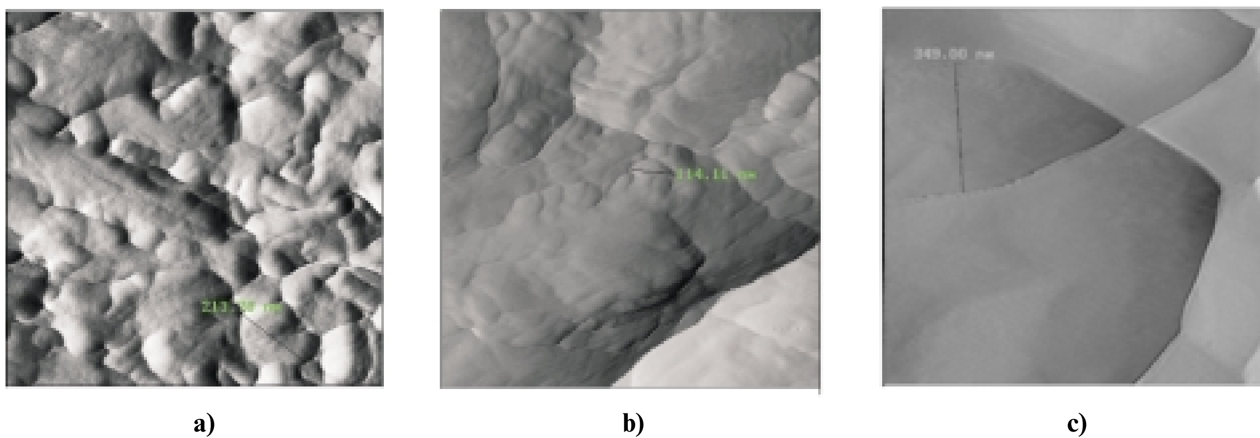
ZnS:Cu/Si

140 120 100 80 60 40 20 0

200 400 600 800 1000 1200 1400 1600 1800

I II III

Fig. 3. The AFM images of ZnS:Cu films surfaces on glass and silicon substrates: nucleating layers (I), films with thicknesses of some tenths of micrometer (II), films with thicknesses of 8 µm. The scan sizes are 5×5 µm, Z-range is 0.6 µm. The histogram of grain size distributions for ZnS:Cu/Si structure is shown at the bottom.



a) **b)** **c)**

Fig. 4. The deflection mode AFM-images of ZnS:Cu/$BaTiO_3$ surface: initial surface (a); surface after annealing at 850 °C (b); surface after annealing and simultaneous Ga doping (c). The scan sizes are 1×1 µm, Z-range is 10 nm.

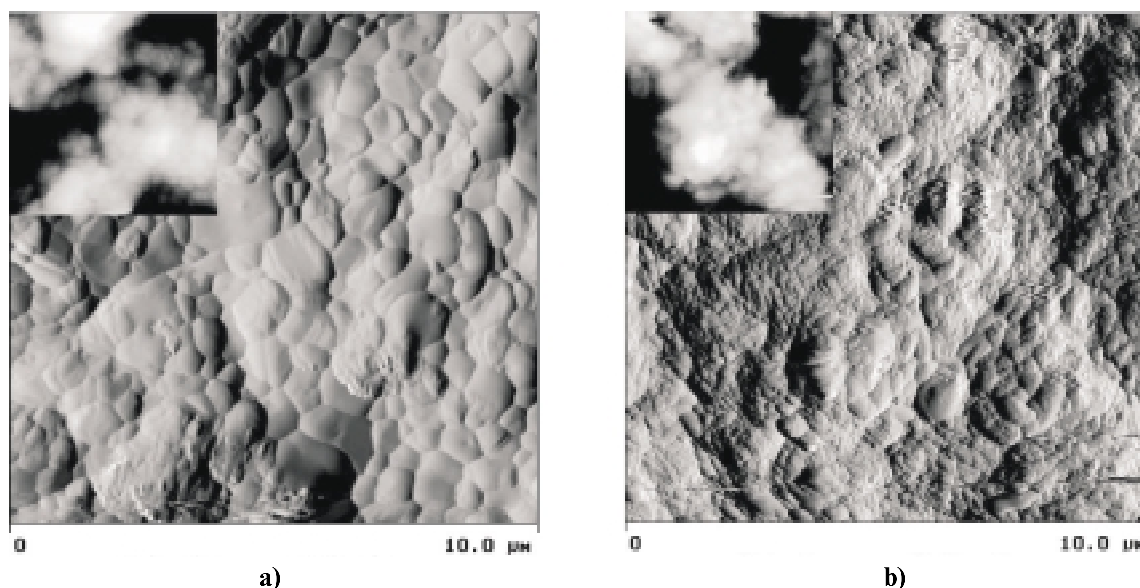


Fig. 5. The deflection mode AFM images of Ga-doped ZnS:Cu/$BaTiO_3$: surface doped from homogeneous Ga source (a); surface doped from nonuniform Ga source (b). Scan sizes are 10×10 µm, Z-range is 10 nm. Topography of the same surface area is shown on the insertion (Z-range of 0-1.5 µm is mapped as gray colors from black to white).

Conclusions

During examinations of ZnS:Cu films at different deposition stages as well as after additional annealing the following results were obtained:

1. At deposition of ZnS:Cu from the ZnS target with hexagonal structure, we obtain films with the ZnS cubic structure textured in <111> direction.
2. For our cases of substrates, the ZnS:Cu/$BaTiO_3$ structure is the most optimum for the new method of annealing with simultaneous doping by Ga.
3. The type of Ga vapor source determines uniformity both grain sizes and Ga-distribution in the film at annealing with Ga co-doping. Such variated distribution leads to various luminescent properties in different areas of films.
4. At the non-vacuum annealing and Ga doping, the size of grains is enlarged, which leads to increase of PL and EL luminosity of ZnS:Cu film and also to diminishing threshold voltage of EL excitation.

Thus, structural investigations of ZnS:Cu luminescent films, deposited by the electron-beam technique and annealed with Ga co-doping by the new non-vacuum method showed that this method can be to used for making thin-film luminescent structures with high brightness and low threshold voltage. This method is economical and high effective. All abovementioned allows stating that it is promising method for application in the field of phosphors manufacturing for various purposes.

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