

ELECTROLUMINESCENCE BRIGHTNESS AND LUMINOUS EFFICIENCY OF ZnS:Mn DOPED WITH KCl

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ABSTRACT

The electroluminescence (EL) characteristics of ZnS:Mn doped with KCl for alternating current thin film electroluminescent devices deposited by a RF sputter system from ZnS and Mn targets are investigated. Measurement of EL brightness and luminous efficiency (η) was carried out. K is uniformly distributed through the 1 μm ZnS film after 5 minutes anneals at $T \geq 600^\circ\text{C}$, while Cl requires an anneal at $T \geq 700^\circ\text{C}$ before diffusion results in a uniform concentration. Upon annealing at 700°C for 5 minutes, the equiaxed grains were consumed by growth of the columnar grains, and growth of the columnar grain diameter is enhanced by the presence of KCl. The mixed cubic and hexagonal atomic stacking observed in as-deposited films became more cubic upon annealing with KCl co-dopants. K^+ diffuses by an interstitial mechanism and it occupies an interstitial site in the cubic structure where it acts as a donor, similar to substitutional Cl^- . ZnS:Mn co-doped with KCl shows significant improvement in EL brightness and luminous efficiency. It was concluded that the improved EL properties result from both improved crystallinity and modification of point defects and space charge in the ZnS:Mn, KCl films.

1. INTRODUCTION

The standard alternating current thin film electroluminescent (ACTFEL) device consists of an phosphor layer sandwiched between two insulator layers which are contacted with a transparent and an opaque electrode, respectively. ZnS:Mn is one of the most widely investigated thin film phosphors for electroluminescent (EL) devices with an emission peak at 584 nm. The ZnS:Mn thin films could be deposited by different techniques, such as electron beam (e-beam) evaporation, co-evaporation, thermal evaporation, sputtering, atomic layer epitaxy (ALE), metal-organic chemical vapor deposition, multi-source deposition, and halide-transport chemical vapor deposition [1, 2].

The EL performance of the ACTFEL devices is a strong function of the crystallinity of the phosphor layer, the insulator/phosphor interface properties, space charge in the phosphor, the nature of the luminescent centers, and their coordination in the host crystal lattice [3].

In ZnS:Mn system, Mn^{2+} easily substitutes in the Zn^{2+} lattice because of their comparable ionic radii (0.80 vs. 0.74 Å) [4] and the same valence. The Mn^{2+} concentration for the optimum EL brightness and efficiency is 1–2 mol.% [5]. Since the transition of Mn^{2+} occurs within 3d orbitals, which are not shielded from the ZnS host lattice, the crystallinity of the ZnS strongly impacts the brightness and luminous efficiency of the ACTFEL devices. Point and extended defects may provide non-radiative relaxation sites, thereby reducing EL emission and efficiency. It has been shown that KCl introduced by ex situ doping via diffusion during rapid thermal annealing (RTA) results in remarkable improvements in EL brightness and efficiency [6]. The changes in ZnS crystallinity during this process has been investigated in this study.

2. EXPERIMENTAL

The devices used in this study were normally configured ACTFEL devices consisting of a Corning 7059 glass substrate coated with 300 nm of indium tin oxide (ITO) and 220 nm of aluminum titanium oxide (ATO) layers prepared at the Faculty of Nuclear and Physics Engineering at Prague. The ZnS:Mn phosphor layer was deposited using two independently operated RF planar magnetron sources with a dense CVD intrinsic ZnS and a metal Mn target, respectively. The ZnS source was operated continuously at 150 W, while the Mn source was operated at 60 W, 5% duty cycle. For co-doped samples, KCl was thermally evaporated onto the surface of the phosphor layer at room temperature, and diffused in via RTA by heating to various temperatures for 5 min in a 99.999% nitrogen flow. After any residual KCl was rinsed off by deionized water, 200 nm aluminum reflective electrodes were deposited by thermal evaporation at a chamber pressure $<2.66 \times 10^{-4}$ Pa. Grain morphologies and defect structures were characterized using transmission electron microscopy (TEM) on a JEOL 200CX, operating at 200 kV. A frequency of 50 Hz was used for all testing. EL efficiency was measured using a Sawyer-Tower circuit [7].

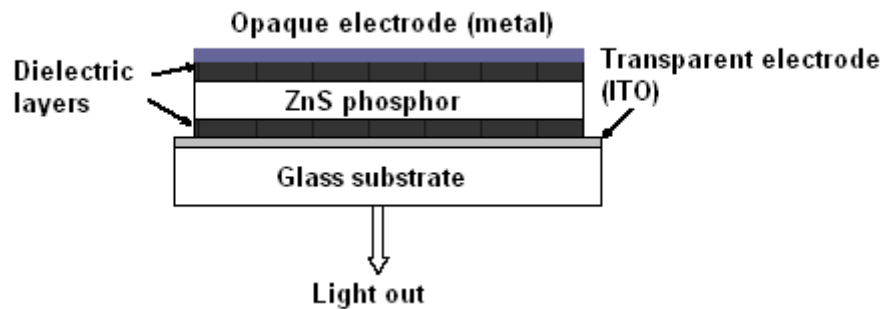


Fig. 1. Schematic of EL device stack used in this study.

3. RESULTS AND DISCUSSION

The grain structure from as deposited ZnS:Mn is shown in Fig.2 by TEM photomicrographs taken from an ACTFEL device. In Fig. 2a, a layer of very fine equiaxed grains (10 nm grain diameter, 100 nm thick) is observed close to the insulator/phosphor interface. The grain boundaries of most of the columnar grains in the balance of the cross section are barely definable. The columnar grain diameter measured by the mean linear intercept from plan-view TEM photomicrographs is 90 nm. Contrast bands in the columnar grains are obvious. After an RTA at 700°C for 5 min, KCl co-doped ZnS:Mn phosphor exhibited en-

hanced columnar grain growth (to a grain diameter of 190 nm) which also consumed the equiaxed grain layer at the ZnS/ATO interface (Fig.3). The density of the contrast bands was still high in this sample, independent of whether or not KCl was co-doped. Finally, KCl co-doped ZnS:Mn thin films annealed to $T \approx 900^\circ\text{C}$ resulted in very large grains which approached equiaxed geometries with diameters $>1 \mu\text{m}$.

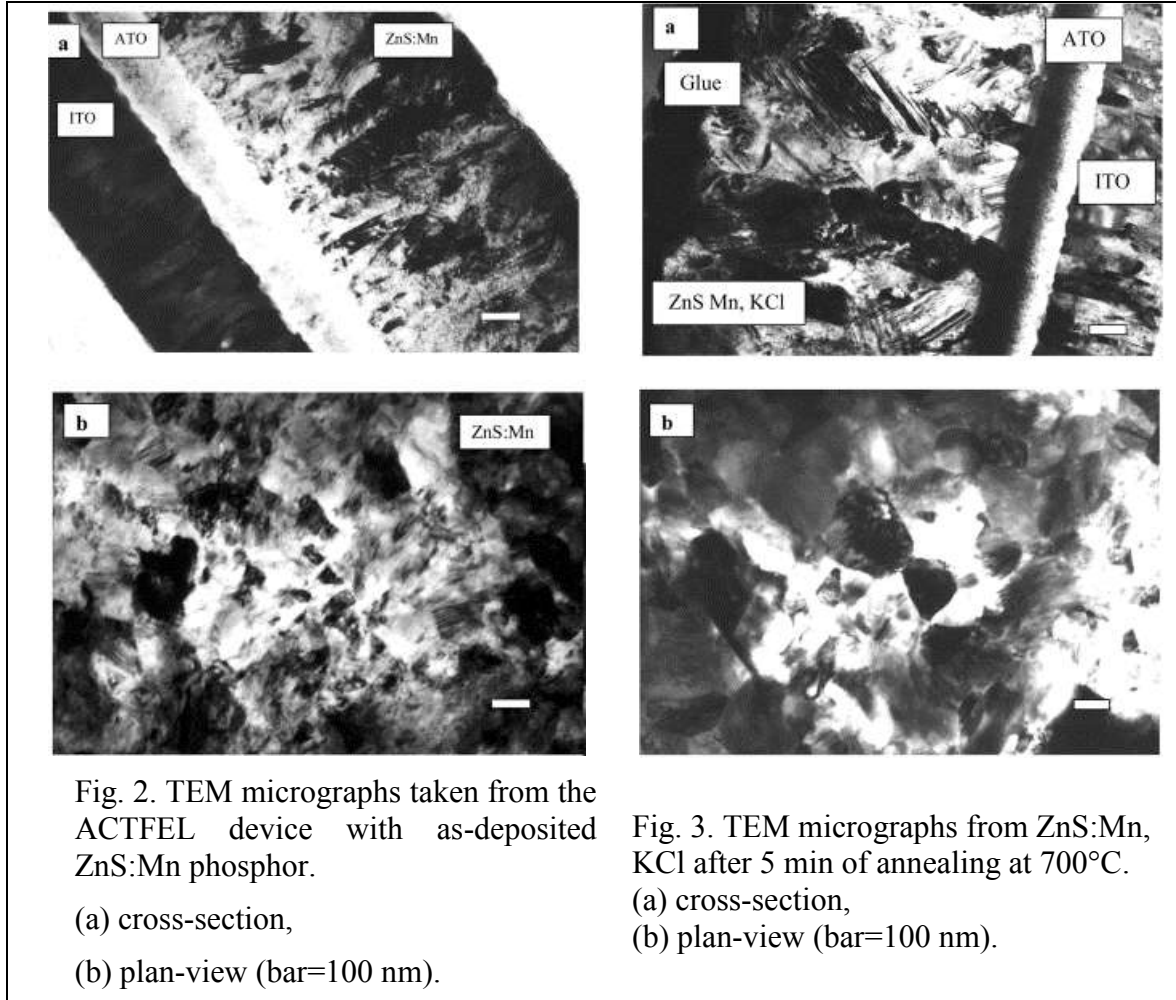


Fig. 2. TEM micrographs taken from the ACTFEL device with as-deposited ZnS:Mn phosphor.

(a) cross-section,
(b) plan-view (bar=100 nm).

Fig. 3. TEM micrographs from ZnS:Mn, KCl after 5 min of annealing at 700°C.

(a) cross-section,
(b) plan-view (bar=100 nm).

The luminous efficiency and brightness from samples as-deposited or annealed at 700°C with or without KCl are plotted in Fig.4. In all cases, the brightness first increases almost linearly with the applied voltage, then tends to saturate in the high voltage regime. This behavior is characteristic of ZnS:Mn devices [8]. Data in Fig.4 also show that the slope of the $B-V$ curve from KCl doped sample is larger than for undoped samples, indicating a sharper turn-on behavior. Neither annealing nor incorporation of KCl changed the color of ZnS:Mn thin films, since all the EL emission spectra exhibit a peak at 580–584 nm, and no changes in CIE coefficients are detected.

Luminous efficiency is defined as the brightness divided by the consumed power. Because the Mn^{2+} concentration was optimized and uniformly distributed in as-deposited films, the low brightness and relatively high threshold voltages are ascribed to the heavily defected sputter deposited microstructure. The 100 nm thick layer of 10 nm equiaxed grains (see above) could be a ‘dead layer’ for hot electrons. For 2–3 eV electrons, the mean free path is $\approx 10 \text{ nm}$ based upon numerical Monte Carlo simulation [6]. This is equal to the average grain size in the equiaxed layer. If the grain boundaries were hot electron scattering cen-

ters, they would reduce the number of ‘hot’ electrons and therefore the EL intensity. In addition, the poor resolution of grain boundaries in as-deposited films suggests that a large concentration of point defects may be present. It is logical to assume that these point defects would lead to both scattering and non-radiative recombination, further reducing EL brightness and efficiency. This is especially true since the 3d orbitals of Mn^{2+} ions, where the recombination occurs, are not shielded from the ZnS host. The point defects could create relatively shallow band gap states that would allow injection of charge into the ZnS conduction band at low fields. This hypothesis is consistent with the weak ‘turn-on’ shown in Fig.4. The increase in EL brightness upon annealing without KCl is ascribed to improved crystallinity at both the ATO/ZnS interface and in the columnar grains, as evident from grain growth and improved resolution of the grain boundaries. Although no direct experimental observations of the type and density of point defects are available, most defects should be annealed out after 5 min at 700°C, since this corresponds to a homologous temperature of 0.6 (i.e. is at 60% of the melting point of ZnS in K). At this homologous temperature, rapid diffusion is expected to lead to the destruction of point defects and reduction of non-radiative pathways, with consequent improvement in brightness.

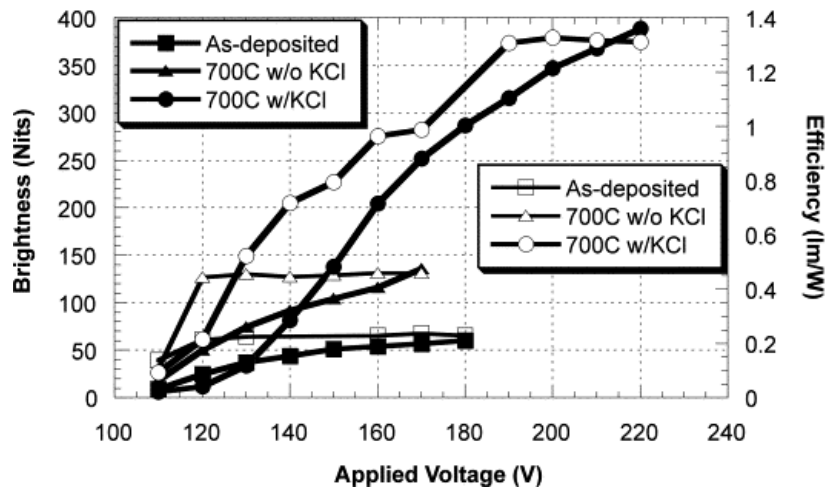


Fig. 4. Effects of RTA and KCl co-doping on EL brightness (solid symbols) and luminous efficiency (open symbols).

Annealed samples doped with KCl exhibited higher threshold voltages, significantly improved EL brightness, and a much sharper turn-on behavior. The small equiaxed grains at the ZnS:ATO interface were eliminated and even more grain growth was observed than for anneals without KCl co-doping. These further improvement in crystallinity with KCl co-doping during annealing would be expected to lead to better EL brightness, because it also results in less space charge, which is believed to be associated with reduced hole trapping at $V_{Zn}-Cl$ complexes. Less space charge should result in hotter electrons with higher energy, which results in improved EL efficiency. Improved crystallinity cannot explain the increased threshold voltage and sharper turn-on, which must be related to the existence of K^+ interstitial and/or Cl^- substitutional ions. Both K^+ interstitials and substitutional Cl^- in ZnS:Mn can be donors. If their energy states are sufficiently far from the conduction band, a relatively high electric field is required to ionize them. In addition, since they should have a well defined energy state, a much sharper turn-on behavior is expected. The extra donors increase the hot electron population, which contributes to higher EL brightness.

4. CONCLUSION

The effects of KCl co-doping on the microstructure and the EL properties of ZnS:Mn phosphors have been investigated. At temperatures of 700°C, incorporation of KCl improves the crystallinity of the ZnS:Mn phosphors by enhancing grain growth in the columnar grains and causing them to consume a 100 nm layer of equiaxed fine grains at the ATO/ZnS interface. In addition, KCl co-doping allows growth of grains to diameters > 1 μm at $T \approx 900^\circ\text{C}$. K diffused through the ZnS film at $T \geq 600^\circ\text{C}$ in 5 min, and exhibits a small activation energy. Based on these observations and its ionic size, it is postulated that K occupies interstitial sites in cubic ZnS, and therefore acts as a donor in the lattice. Co-doping with KCl improves the brightness and efficiency by $\approx 100\%$, and increases the threshold voltage and makes the slope of the $B-V$ plot much larger. The EL data show that while improved crystallinity may reduce non-radiative recombination, the most important effects of KCl co-doping are a reduction of space charge and band bending with a resulting larger, hotter electron population in the EL phosphor.

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